

Control of Emissions from Residential Wood
Burning by Combustion Modification

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CONTROL OF EMISSIONS FROM
RESIDENTIAL WOOD BURNING
BY COMBUSTION MODIFICATION

by

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ABSTRACT

This report describes an exploratory study of the factors contributing to atmospheric emissions from residential wood-fired combustion equipment. Three commercial appliances were operated with both normal and modified designs, providing different modes of burning. Operating conditions included up draft using a grate, up draft using hearth, cross draft, down draft, and a high turbulence mode utilizing a forced draft blower. Fuels used were naturally dried commercial oak cordwood, commercial green pine cordwood, oven-dried fir brands, and naturally dried oak cut into reproducible triangular shapes. Continuous measurements of stack gases included O_2 , CO_2 , CO , NO , SO_2 , and total hydrocarbons (FID) as an indication of the total organic species in the stack gases during batch type operation. Several combustion modification techniques were identified which have an appreciable effect on emission and therefore can be developed and applied to reduce emissions in consumer use. The more promising design modifications include: prevention of heating the inventory of wood within the stove but not yet actively burning focus of air supply into primary burning area with high turbulence, and increase the temperatures in secondary burning regions of the appliances.

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SECTION 1

INTRODUCTION

The use of wood for residential heating is certainly not a new phenomenon. However, this use of wood has increased appreciably in recent years and the trend is expected to continue. It has recently become increasingly apparent that (1) the emissions from residential wood stoves can in some instances constitute a serious environmental problem, and (2) that the technology required to burn wood in small stoves without significant emissions is not now available. Because the use of this renewable energy resource is to be encouraged, it is necessary to develop and apply the technology necessary to make the stoves environmentally acceptable, rather than restrict their use on environmental grounds.

This study was initiated to explore the combustion modification techniques that might be applied beneficially to wood stoves, and more specifically to identify those techniques which show promise of providing a significant improvement in emissions when adequately developed and applied. The focus of the effort is on naturally-drafted, hand-fired radiant stoves, as these constitute the majority of units used extensively for residential heating.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

As the result of this study, there appear to be several combustion modification techniques available to reduce the gas emissions from wood stoves, with varying degrees of probable effectiveness, and different levels of acceptability to residential stove builders and operators. These techniques are briefly summarized below, noting whether a modified stove design is required, special operator techniques are required, or specific as a guide to indicate the more promising combustion modifications which should be developed in more detail to justify extensive reduction to practice by stove users. Modifications are presented first which prevent gas composition formation in the magazine (A), and in the primary combustion region (B), followed by those which cause previously formed gas combustion to be destroyed within the primary burning zone (c) or in the secondary combustion zone (D). Finally, a few add-on devices are identified (E) which may or may not be incorporated into the stove, but can reduce gas composition from the complete heating system. In each category the modifications are presented in decreasing order as to their expected likelihood of being effectively reduced to practice.

To apply most of the modifications noted below, and all those involving destruction of previously formed pollutants, will require stove design alterations. These are generally beyond the ability of most residential stove operators. A few very significant gas composition reductions by operator technique modifications can be obtained using existing stoves, if the operators are sufficiently motivated to change their procedures or characteristics of the fuel they burn.

A. PREVENTION OF GAS COMPOSITION FORMATION IN FUEL MAGAZINE

Wood is placed within a wood stove in a quantity to support burning for a prolonged period. Considering that the magazine receiving this wood is usually an integral part of the combustion chamber, the entire

charge of wood can become heated, resulting in pyrolysis off-gassing. When these gases leave the magazine and the stove unburned, they contribute directly to the organic gas composition of the stove. Several techniques to reduce this source of gas composition are as follows:

- (1) All the wood inventory within the stove should be kept at a low temperature until active local burning is started. This will preclude extensive pre-burning pyrolysis. Primarily design modifications are needed, possibly with an altered operator technique.
- (2) Small charges of wood should be placed in the stove at one time in order to prevent extensive pre-burning pyrolysis. This is an operator characteristic which at first consideration is undesirable to an operator who wants long burning periods with no attention. It should be effective in most existing stoves as a means of reducing emissions.
- (3) After combustion has been established, only large pieces of wood should be fired, consistent with desired burning rate maintenance. This is a fuel characteristic that may require more frequent attention or demanding operator techniques. By this means pyrolysis can be kept to a minimum in existing designs of stove.
- (4) Very low moisture fuel, kiln dried, should be discouraged, particularly when placed in large quantities in a magazine. Pre-burning pyrolysis is more rapid and leads to high gas composition. This fuel characteristic is less of a problem with conventional air dried cordwood, but imposes special operator demands when very dry wood is to be burned in a low-gas composition manner.
- (5) Devolatilized wood such as charcoal is a highly recommended fuel, generally producing low gas composition of CO and organic materials. This fuel characteristic is limited by fuel costs to the consumer, but is suitable for use in some wood stoves.

B. PREVENTION OF EMISSIONS FORMATION IN COMBUSTION REGION

The wood that is actively burning in a stove is subjected to a restricted supply of air as a means of control of the burning rate. This deficiency of air can result in incomplete burning of the fuel constituents, permitting the emission of reduced and incompletely oxidized materials into the stack and ultimately into the environment.

- (1) High burning rates should be maintained as an operator technique to reduce gas composition. This may become objectionable to the operator, as being incompatible with comfort heating when considering the comfort heating demands and the heating capacity of the stove.
- (2) Primary air should be directed specifically to a limited burning region or volume, to preclude widespread burning with the available supply of air. This is a design factor that may be difficult to accomplish with a fixed geometry design suitable for a wide range of burning rates, but might be accomplished with simple discrete geometry changes made by the operator within design limits.
- (3) A high turbulence level should be maintained in the active burning area, by using stove design techniques. The use of an air blower with tailored air ducting should achieve this objective. A "within-firebox" source of air to the blower might be used to minimize the hazards of blower failure and to provide modulated operation during a batch type of burn. The high turbulence level assures improved mixing and thorough combustion with less stratification of air and combustible pyrolysis products.
- (4) Excess fuel should be eliminated from the primary burning area as a means of preventing severely fuel-rich combustion. This situation could partially be achieved by limiting a continuous flow of fuel feed into the area to match the desired burning rate. This situation is generally not attainable with stick wood but could be accomplished with a stove designed specifically to burn a free flowing form of wood, such as pellets. This drastic design approach could essentially provide fuel-controlled burning.

- (5) High temperatures should be maintained in the active burning area to promote rapid and complete burning of fuel. This design characteristic should minimize incomplete combustion associated with quenching of partially burned fuel, and can be improved by use of insulating refractory materials enclosing the combustion chamber.
- (6) An abrupt reduction in the rate of primary air supply to an operating stove does not simultaneously reduce the rate of pyrolysis of the wood being burned. The sustained gas evolution by pyrolysis, coupled with the reduced supply of air, increases the gas composition of unburned or partially oxydized fuels. This phenomenon should be avoided, whether it be by an abrupt operator technique or by severe cycling of a thermostatic control device.

C. DESTRUCTION OF EMISSIONS IN PRIMARY BURNING ZONE

The flames in the area of active wood burning are fed by two sources, combustible emissions from the adjacent wood surfaces, and any combustible products carried into this area from elsewhere in the stove. If this local burning is complete, it will consume all the organic materials and combustibles which would otherwise be emitted. The following approaches should improve the completeness of burning in this primary burning zone.

- (1) Increased turbulence in the primary burning zone will promote the complete burning of pyrolysis products released directly into the flame region, thus eliminating some or all of the products of incomplete burning. This requires a design change similar to that noted in technique B-3 above.
- (2) Increase the temperature in the primary burning zone as in technique B-5 above.
- (3) Increase the residence time at active combustion conditions while maintaining temperatures and turbulence levels. This is a design approach that may also become practical with a blower system as in technique B-3 above.
- (4) Pyrolysis products from the magazine region should be ducted only into an active burning region where adequate air supply and temperatures will promote complete combustion. This is a design consideration.

- (5) Develop a down draft design of combustion chamber that will assure that all gas flow through the wood inventory travels in the direction contrary to the progression of the burning through the wood. When down flow of air is used, a reduction in the bed area should accommodate reduced burning rates while maintaining the counter flow phenomenon.

D. DESTRUCTION OF EMISSIONS IN SECONDARY COMBUSTION ZONE

Most stoves include a region or zone within the stove where secondary combustion can occur, and provide a supply of secondary air to support this combustion. When secondary combustion is achieved, a significant reduction in emissions can be obtained. The following procedures include techniques to increase the likelihood of achieving this combustion, and extend the range of conditions that will support it.

- (1) The temperatures in the secondary combustion chamber should be kept high to broaden the range of gas mixtures that will permit combustion. This is a design characteristic of the stove using insulation and proximity of the secondary air inlet to the inlet of the primary combustion chamber to improve chamber heat retention.
- (2) The secondary air should be heated to provide the same effect as noted in D-1 above, and avoid quenching secondary combustion that might otherwise occur. This design factor can be accomplished by within-the-stove heating of secondary air prior to mixing with primary combustion products.
- (3) The envelope of gas mixtures that will permit combustion of primary combustion effluents and secondary air can be widened by increasing the combustibles content of primary effluents. This shift of operation towards gasification in the primary combustion chamber could ultimately result in clean burning with reduced emissions if the secondary combustion was maintained under all operating conditions. This requires a major design alteration, possible with the operator exercising effective control over both primary and secondary air supply.

- (4) An auxiliary ignition source could be provided in the secondary combustion space, possibly supplied by an auxiliary fuel, an electric ignition source (glow plug) or a "pilot light" fed from the primary combustion itself. Such a device to assure ignition would be primarily a design oriented technique, which might be augmented by stove operator initiation, monitoring or control.

E. ADD ON SYSTEMS FOR EMISSIONS CONTROL

Modifications exterior to the fuel and firebox design can also be effective. Two techniques are suggested which should significantly and directly reduce emissions. A third add-on device is possible that can indirectly reduce emissions. These techniques can be applied as separate devices between the stove and stack, or by major design modification included within a stove envelope.

- (1) Catalytic afterburners are being developed and applied to wood stoves with at least one new design stove currently being marketed. By reducing the temperature at which combustion can be initiated, and by conserving the heat released to maintain the combustion, the catalytic unit might significantly reduce emissions under many but not all conditions of burning. This constitutes a design modification although visual monitoring by the operator would be advisable.
- (2) A separately fueled afterburner could be developed, preferably using a gaseous fuel. A significant increase in equipment cost, auxiliary fuel use, and heat delivery rate will probably result from such a design change.
- (3) A greatly increased heat storage capacity can be added to a stove, permitting a higher burning rate operating for short time periods, yet still providing a near-steady delivery of heat to the living space. This modification permits all burning to be at high rates, with the correspondingly reduced gas composition. Heat could be stored as sensible heat such as with water or solids (stone or metal), or as latent heat such as with Glauber's salts or other phase change material.

SECTION 3

WOOD AS A FUEL

Currently wood combustion provides about 1.5 Quads* of energy to this country yearly, with about 0.3 Quads used for residential heating. This residential use of wood should increase to 1.0 Quad in the next 20 years, and actions are planned in support of this goal. Practically all of the residential wood utilization is now based on cordwood which is widely available, with most of the burning in residential stoves and fireplaces. Wood stoves are increasingly being recognized as the more efficient device, and the use of wood stoves has increased rapidly in recent years as the prices of other residential fuels, especially oil, have increased at a very high rate. Central furnaces will probably become more prevalent as commercial distribution of wood is developed, especially processed wood such as pellets. Probably most of this residential wood is now burned in stoves and enclosed fireplaces, instead of open fireplaces due to the increased efficiency and longer burn times for stoves and forced air units. It has been estimated (1) that the residential heating with wood might grow from the present 4 million homes to as many as 15 million by 1985. Due to the general recognition that airtight stoves provide higher efficiencies than open fireplaces, the increase will probably be primarily in this type of stove.

Various other forms of wood are available commercially in limited quantities and in limited areas of the country. These include sawdust as an industrial waste product, wood chips, and wood processed into pellets or densified logs. Although growing, the use of these other forms is still considered to be small compared to conventional cordwood, for hand fired appliances.

The environmental aspects of increasing residential wood burning fall into two arenas: harvesting with resource depletion considerations, and burning with objectionable atmospheric emission considerations. The former

* 1 Quad = 10^{15} Btu

can be controlled by using proper silvaculture or forestry management techniques which have been demonstrated by the forest products industry and local farm agents for many years. The objectionable emissions, however, are not widely recognized, and the technology for reducing or eliminating objectionable emissions is not well developed. Both health and visibility aspects of the emissions are significant.

PROPERTIES OF WOOD

Wood is available as a fuel in most parts of the country, usually in the form of split logs and/or sticks, known as cord wood for residential applications. The principal variables in cordwood are hard-wood species or soft-wood species, and air dried (cured) or green (freshly cut). Dry hardwoods have a slightly lower heating value than dry soft-woods which generally have a higher resin content. More important to heating value is the moisture content, which varies between about 5 percent for very dry wood to over 50 percent for freshly cut wood, with 20 percent being typical for air dried wood.*

The chemical composition of dry wood as measured in percent carbon, hydrogen and oxygen is very similar for hardwoods and softwoods. The elemental content is typically about 40 to 52 percent carbon, about 6 percent hydrogen, and 40 to 44 percent oxygen. The cellulose content does vary as follows:

	<u>Hard Woods</u>	<u>Soft Woods</u>
Cellulose	43	43
Hemicellulose	35	28
Lignin	22	29

When the woods are pyrolyzed the cellulosic materials break down most easily into volatiles whereas the lignin materials are more char forming.

Cellulose is a high molecular weight polymeric carbohydrate containing nonaromatic glycoside rings joined by oxygen. Cellulose products thus do not directly contain aromatic species, but can contain many simple hydrated species. The formation of long chain or fused ring species may require more severe conditions than those required to initiate simple pyrolysis.

* The moisture content of wood is measured and reported on either of two bases: weight of moisture per weight of dry wood, and weight of moisture per weight of moist or as-fired wood. The latter is used in this discussion.

SECTION 4

COMBUSTION CHARACTERISTICS OF WOOD

The combustion of wood is generally recognized as involving three processes or phases: moisture evaporation, pyrolysis with subsequent space burning, and surface char burning. These processes occur successively on any local particle of wood, but in normal combustion systems there is an overlap with all three processes occurring simultaneously within the combustion chamber. This overlap is especially significant when prolonged burning eliminates water early and the other two continue.

EVAPORATION

The amount of moisture evaporation depends on the moisture content of the fuel as fired, which can vary from over 50 percent for some green wood to essentially zero for oven-dried wood. As the wood is heated this moisture is evaporated, beginning at the outer surface where the heat is applied. As heating progresses the moisture from the center of the piece diffuses as vapor through the outer material. In large pieces this outer material may have been heated appreciably above the steam point, even to temperatures at which pyrolysis or char burning occurs. This efflux of water vapor to the surface of the wood retards heat flow into the wood, both from the steam's sensible heat gain and by a thickening effect on the gaseous boundary layer through which the initial convective heating usually occurs. This type of cooling thus retards the burning of wood, especially when large pieces are used and when moisture content of the wood is high.

PYROLYSIS

Pyrolysis of the wood starts as the local temperatures rise above 100°C, with low temperature pyrolysis being endothermic. These product gases contain H₂O, CO₂, CO, CH₃COOH, HCOOH, and others. Although the off-gas

has a positive heating value, the steam and CO_2 content of this initial discharge reduces the heating effectiveness. As the local temperature exceeds about 280°C , the pyrolysis becomes exothermic, temperatures increase without local oxygen consumption, and larger quantities of gas are obtained. This off-gas contains additional heavy organic molecules and entrained particles (droplets) of wood tars. The rate of pyrolysis, especially at the lower temperatures, is closely dependent on the rate of heat transfer to the pyrolyzing wood.

The quantity of pyrolysis off-gas (including entrained organic liquids) is increased appreciably by the rate of pyrolysis. Very slow pyrolysis leaves half of the original dry weight of the wood as a char, whereas very fast pyrolysis reduces the char residue to 13 percent of the original dry weight (2). The total heating value of the off-gas (Btu/lb wood) from rapid pyrolysis is thus much higher than that from slow pyrolysis. The ignition temperature of this off-gas from wood pyrolyzing is about 600°C after being mixed with air. Thus, burning requires either (a) an adjacent flame or hot surface, such as other localized burning, or (b) a surface layer through which the gas diffuses which is sufficiently hot that the 600°C ignition temperature is retained after mixing with adequate air. The latter is likely only when the gas evolution rate from internal evaporation and pyrolysis is relatively low and/or the radiant heating of the surface is sufficiently high.

This off-gas burns vigorously in a flame when it passes through the surface of the wood allowing reaction with the oxygen supporting the combustion. Should there be insufficient oxygen, insufficient turbulence to assure thorough mixing, or inadequate residence time at flame temperatures, some fraction of these pyrolysis off-gases can leave the combustion area incompletely burned. This incompletely burned fuel can contain either the original off-gas species or original species thermally altered into other species.

CHAR FORMATION AND BURNING

The third phase of wood burning occurs when the local wood has been thoroughly pyrolyzed, leaving a porous carbonaceous char. This char burns at its surface when temperatures are adequate and sufficient oxygen diffuses to the surface. This char burning is essentially flameless except for (a) slight

gaseous hydrocarbon evolution from the small amount of hydrogen residual in the char, (b) the partial oxidation to CO by oxygen at the exposed active surfaces and subsequent burning of the CO, and (c) the watergas reaction with steam from internal moisture vaporization. Although the ignition temperature of pure carbon is high, fresh charcoal can sometimes ignite at much lower temperatures than the pyrolysis off gases (2).

The char has a lower thermal conductivity than the original wood. Thus, slow burning of a large piece of wood, resulting in a thick outer char layer, is made even slower by the reduced heat flux to the interior. The hot char layer may also change the effluent gas composition, as noted above, by reacting with the water vapor to form CO and H₂ (water gas reaction), and also by cracking some of the heavier hydrocarbon gases and liquids from the pyrolysis zone.

BURNING PROGRESSION

Table 1 shows the progression of the several phenomena that typically take place during the progressive burning of a piece of wood. The sequence of events vary in relative timing at different locations in the wood depending on many factors. The whole process is accelerated by high incident heat flux, small piece size, and low moisture content. Wood size and moisture content particularly affect interior change rates. The surface phenomena are predominantly affected by radiant heat flux, oxygen supply conditions, and gas evolution rates (moisture and pyrolysis products).

WOOD CONSTITUENTS RESULTING IN ATMOSPHERIC POLLUTANTS

There are no constituents in wood in large quantities that are recognized as being inherently objectional sources of pollution. The S and N contents are generally less than 0.01 and 0.1 percent, respectively. With complete conversion to SO₂ and NO, the emissions would be below 0.025 and 0.27 lb/10⁶ Btu (12 ppm SO₂ and 276 ppm NO), respectively. Toxic metals such as lead and mercury do not occur in large enough quantities to constitute a hazard. Wood ash is normally considered a beneficial soil additive, but must be disposed of with care due to its alkalinity.

TABLE 1. TYPICAL PROGRESSION OF LOCAL PHENOMENA
IN WOOD LOG BURNING

LOCATION OF PHENOMENON	Log Introduction → → → Time Progression			
DISTANCE FROM SURFACE	Radiation influx	Radiation influx	Radiation influx	Radiation influx
NEAR TO SURFACE	Convection influx	Convection influx reduced by steam efflux	Convection influx is reduced by efflux of pyrolysis products and steam	Convection influx Unattached luminous flame
SURFACE PHENOMENON	Heat influx	Heat influx Steam efflux	Heat influx Steam and pyrolysis products efflux	Increased heat influx Steam, pyrolysis gas, and liquids efflux
SURFACE MATERIAL	Sensible heating	Moisture evaporation	Low temp. pyrolysis	Exothermic pyrolysis
SUBSURFACE MATERIAL	No change	Sensible heating	Moisture evaporation	Low temp. pyrolysis
INTERIOR MATERIAL	No change	No change	Sensible heating	Moisture evaporation
CORE, CENTRAL MATERIAL	No change	No change	No change	Sensible heating
	Time Progression → → → Burnout			
Radiation flux near balance	High radiation outflow	High radiation outflow	High radiation outflow	Radiation ceases
Intense luminous flame	Decreasing luminous flame	Reduced flames less luminous	Diffusion control of surface burning	--
Radiation much increased Large gas efflux	Highly radiant surface Gas efflux reduced	Char burning Attached blue flame Highly radiant surface	Char burning No flame Highly radiant surface	--
Char formation	Pyrolysis products cracking and steam dissociation within char layer	Surface lost	Surface lost	Surface
Exothermic pyrolysis	Pyrolysis products	Char burning	Surface lost	Surface lost
Low temp. pyrolysis	Exothermic pyrolysis	Pyrolysis products cracking	Char burning	Surface lost
Evaporation	Low temp. pyrolysis	Exothermic pyrolysis	Char burning	Char burnout

The organic constituents of wood, cellulose and lignin, are themselves considered non toxic, but their thermal decomposition or pyrolysis products contain several objectional species including aldehydes, phenols, and creosols. In some cases polycyclic aromatic hydrocarbons (PAH) can be formed. All of these are of concern in the atmospheric emissions.

Two mechanisms for formation of objectionable emissions from wood burning are

- Pyrolysis product release from the wood which never encounters conditions of temperature and oxygen concentration between the pyrolysis site and the stack which satisfy the requirements of complete combustion.
- Incomplete burning due to excess fuel and insufficient oxygen in active areas of burning.

It is to be noted that both mechanisms can occur at high temperatures, and both mechanisms can occur while appreciable oxygen remains in the flue gas. When the temperatures are high enough to initiate combustion, and sufficient oxygen is present, the combustion can go to completion, consuming all of the organics. The contribution of secondary combustion to eliminate these objectional species is discussed later.

Organic emissions resulting from incomplete burning of the wood and its pyrolysis products thus consist of a mixture of chemical species. Some may leave the stove in condensed form, and additional species becomes condensed into and onto particulates or onto the walls of the stack as the gases cool. The particulate mass in the stack at any point of sampling depends not only on the quantity and distribution of organic species carried in the flue gas, but also significantly on the stream temperature at the point of particulate separation from the gas. The logical mechanisms of ash carry over into the stack, suspension burning of fine solid wood particles and aerodynamic entrainment from the bed, are both expected to be ineffective. Thus, the condensed organic species are presumed to constitute the bulk of the stack particulates.

PRODUCTION OF PAH IN WOOD COMBUSTION

Polycyclic aromatic hydrocarbons (PAH) have been identified in wood combustion products. Mechanisms proposed for PAH production from pyro-synthesis and combustion include: (1) polymerization of small organic fragments under reducing conditions: at temperatures above about 400°C (750°F) organic compounds are "cracked" to small reactive fragments that condense into aromatic species with a subsequent gain in free energy over condensation into their paraffinic analogs, (3-5) and also, (2) a pyrocombustion synthesis of PAH can occur from condensation and rearrangement of poly-acetylenes (6). Figure 1 shows a primary pyro-combustion mechanism proposed for PAH production from "cracked" organic molecules.

Several researchers have also investigated the pyro-combustion reactions of cellulose and lignin. These reactions in tobacco leaf materials have been extensively studied and give a valuable literature base to show how a species similar to wood fuel behaves at flame temperatures. In the tobacco case, large weight losses are observed at temperatures nearing the ignition temperatures (400-450°C) (750-840°F) (7,8). Tobacco research has shown that yields of condensible organic material regularly decrease from 400-1000°C (750-1800°F) in pyrolyzed tobacco while recovered PAH increase as the temperature is increased in this temperature range (9). Pyrolysis of cellulose at 800°C (1620°F) (approximately the maximum cigarette burn temperature) produces 1000 times more benzo(a)pyrene (BaP) than the amount measured in main stream cigarette smoke (10). The production of benzo(a)pyrene and other PAH from the cellulose in tobacco has led to several studies (10,11,12).

On warming wood there is a loss of water and volatile species at 60-100°C (140-212°F) and loss of water of hydration at 160-170°C (320-340°F) (13). During the combustion of wood, cell disruption occurs with volatilization, sublimation, pyrolysis, fragmentation and chemical condensation occurring in and around the flame zone. That significant amounts of neutral polycyclic compounds are measured in wood flame effluents is indicative of chemical reactions which have generated the PAH, principally from starting materials of cellulose and lignin which do not originally contain the PAH species measured. Lignin pyrolyzed at 700°C (1290°F) in nitrogen, yields higher levels of phenols and cresols than cellulose under

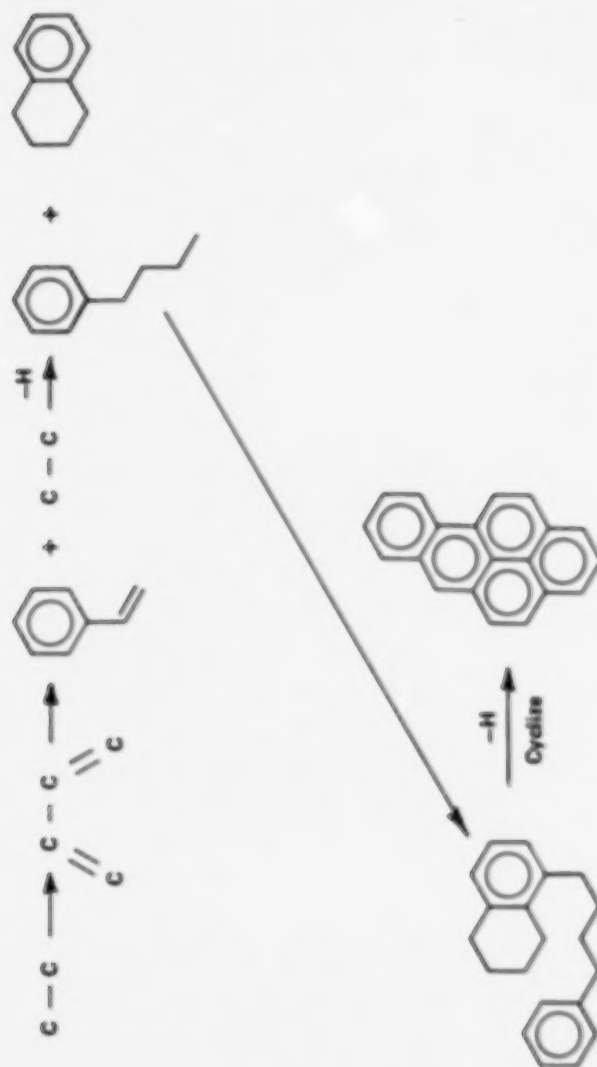


FIGURE 1. PYRO-COMBUSTION TO PRODUCE BENZO(A)PYRENE (2).

the same conditions (14). The maximum phenol formation from lignin is found at 500-600°C (930-1110°F) (15). Studies on the pyrolysis of cellulose have shown that temperatures of 475-420°C (890-790°F) yield low-molecular weight aldehydes, ketones, and aliphatic acids (16,17).

It is important to note that both pyrolysis and combustion of cellulose and lignin lead to the production of PAH, aldehydes, ketones, and cresols. These processes occur at temperatures as low as 400°C (750°F) (3). Since these compounds are not original constituents of wood, their manufacture during the combustion process must be considered under the conditions of available oxygen, temperature, and wood types used in home wood combustion. Further study of this phenomenon might establish conditions of pyrolysis and/or burning at which the PAH species are reduced or not formed.

SECTION 5

WOOD STOVE DESIGN AND PERFORMANCE

There are many designs of wood stoves for residential heating. The radiant heater designed for use in the living space and hand fired with cordwood is the most popular and is the focus of this study. One design of residential wood burning furnace has been developed with improved performance, especially relative to efficiency and emissions. This high turbulence burner, described later, has been included in the study because many combustion modifications have been effectively included in its design.

TYPES OF RADIANT STOVES

There are several options of air flow and fuel flow patterns within the stove that have been adopted in commercialized designs. Figure 2 shows the four generic systems in simplified form. These are described below according to the draft (flow) of primary air. The significance to air pollution emissions is also noted qualitatively for each generic system.

Up Draft

In this conventional system, the primary air flow passes upward through the burning wood. In some stoves the wood, sticks or logs, rest on andirons or on a horizontal air-permeable grate. More often the fuel support (hearth) is inherently not permeable or else the grate openings are effectively plugged with ash. The primary air flow is then introduced near the base of the combustion chamber, i.e., at the wood support level. Buoyance effects resulting from the heating of gases in the burning region induce the flow into the bottom of the wood charge where the primary combustion takes place. The heated gases then move upward through the wood charge. Such stoves can be referred to as true up-draft or diagonal draft, and are characterized by the combustion products moving upwards through the burning

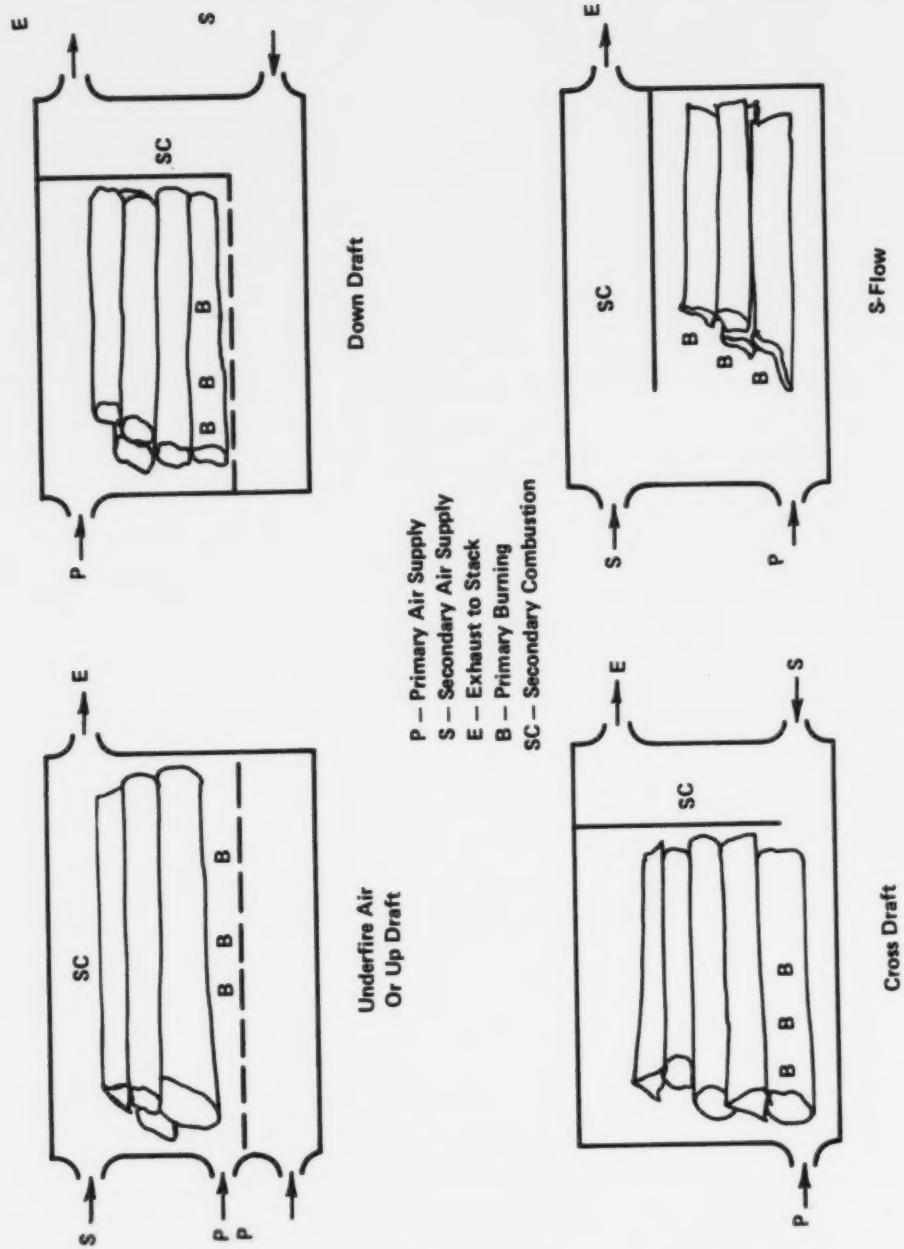


FIGURE 2. GENERIC DESIGNS OF WOOD STOVES BASED ON FLOW PATHS.

pieces of wood, and exiting from the upper parts of the combustion chamber. The products of the primary combustion thus pass through or among the remaining or more recently fed wood. This results in heating and pyrolysis of some of the wood in an oxygen deficient environment. The rate of wood consumption is effectively controlled by the flow rate of this primary air.

A secondary air supply for secondary burning is often provided with the intention that it burn the pyrolysis products either in the portion of the combustion chamber above the charge of wood, or in a separate, distinct secondary combustion chamber. The primary combustion products may be cooled or quenched by the newly fired wood or by heat transferred to the side walls. Even with active flames low in the burning wood, combustion may not be attained in the secondary combustion space.

Simple box stoves are often of this design, especially those which have the primary air inlet at one side (front) of the bottom of an open combustion chamber, and the vent to the stack at the top (rear) of the same open chamber. Although the natural convection within the burning wood charge induces the primary air flow upward through the wood charge, some air can usually bypass this route and support secondary combustion. Simple box stoves and air-tight stoves often have an additional air inlet higher in the stove wall or door to assure this supply of secondary air. As described later this supply of secondary air does not assure secondary combustion, and may actually quench combustion.

Down Draft

This design approach has an historical basis and is used in some stoves today in modified forms. The wood is supported on a grate, with the primary air flow downward through the wood and combustion taking place low in the charge, i.e., at the grate. The principal characteristic and advantage is that the gas flow through the wood is in the opposite direction to the progression of burning through the charge of wood.* Thus, the pyrolysis off-gassing is into the primary air stream as it approaches the hotter, active burning region. This design assures that these pyrolysis products pass through the burning region, and thus promotes burning of the organic compounds. The admission of secondary air immediately down stream of the burning wood thus can aid in the complete burning of pyrolysis gases,

* Some stoves not meeting this description are described and/or advertised as being "downdraft".

as high temperatures can be maintained in this secondary combustion area.

The Vermont Downdrafter stove is a variant of this design, in which the combustion zone is kept small in a fixed location, promoting high temperature burning of all the pyrolysis products. A true downflow combustor is the "Tasso", a residential handfired boiler currently made in Denmark (18).

Side Draft

In the side draft, or cross flow design, the primary air is supplied to one side of the base of the burning wood charge and leaves the primary burning area also at the base of the wood charge. Thus, the evaporated moisture and initial pyrolysis products from the wood prior to its active burning are not released directly into the primary air flow. They are released into a more stagnant region which also serves as a fuel magazine. The convective and radiant heating of the freshly fired wood in this magazine is less than it would be in the main gas flow from the active burning region. By directing the off-gas products only through a hot active burning region, they can be burned when adequate air is supplied and thus are prevented from 'escaping' directly into the stack. This can be either in the primary combustion region or a hot secondary combustion region supplied with additional air.

S-Flow

A large number of small stoves utilize an air flow pattern which involves primary air supply along the surface supporting the wood charge from one end of the combustion chamber, with combustion products leaving the top of the primary combustion chamber at the same side. This design permits slow end-burning of the wood sticks, starting near the air source and progressing slowly away from the source. This flow pattern within the primary chamber is often produced by placing a baffle above the wood charge, directing the products of primary combustion through a restricted area near the air source before entering the stack. Secondary air can be supplied here to support secondary combustion. The location, shape, and size of the baffle

varies among different designs, providing higher velocities and turbulence, and a longer gas flow path but not a longer average resistance time within a given stove envelope.

Many designs of Scandinavian stoves are of this type. These are often called cigarette burning designs, and are conducive to very slow burning.

SECONDARY COMBUSTION

The wood pyrolysis products are released into the primary air stream passing through the wood charge. The pyrolysis rate often exceeds the equivalent air supply as determined by the stoichiometric fuel: air ratio. This results in fuel gases being carried away from the solid fuel in an unburned or partially burned form containing appreciable CO and many organic gases. Most stove designs provide for a secondary air supply to be mixed with the primary stream after the primary stream leaves the wood. Ideally, in this manner the secondary air stream should support complete combustion of all the pyrolyzed fuel, without appreciably increasing the rate of wood consumption.

Figure 3 shows the typical locations for secondary air supply, and the regions where the secondary combustion is intended to occur in each generic design.

This ideal situation is hindered by several phenomena which result in unburned organics and CO leaving the stove unburned:

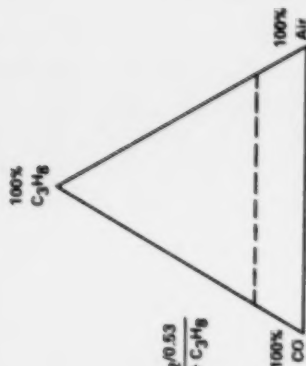
1. The mixing rate and turbulence intensity are limited in natural draft stoves impeding complete secondary burning.
2. The temperatures in the secondary combustion area may be below that necessary for ignition and burning, especially at low rates of burning and in locations in the stove where relatively cold walls quench the flames from the wood.
3. The rate of secondary air flow that would be required to burn the excess fuel gases in the primary flow varies during a burn. Early in the burn period when large amounts of pyrolysis gases are being evolved, insufficient secondary air leaves unburned fuel in the flue gas. Later when the primary burning is largely char burning, excess secondary air might quench the flue gas, resulting in temperatures below those required for ignition.

Considering that essentially all stack particles are organic species and therefore combustible, the occurrence of afterburning or secondary combustion must be recognized as a means of consuming these particles in addition to the gaseous organic species still in the gas phase and the carbon monoxide. This phenomena, when achieved in the stove, not only would reduce emissions, but correspondingly increase the amount of heat released and recoverable from the fuel. Considering these advantages, most stove designs provide for the admission of air to support secondary combustion, and provide a volume or chamber within the stove in which this combustion can occur.

Figures 3, 4, and 5 show the combinations of temperature, CO, organics (calculated as being propane), air, and inerts that satisfy the requirements for ignition and burning. The curves on the tri-axial coordinates bound the region where combustion can occur. It is evident that increased temperatures widen the bounds making combustion more likely, and that increased inerts narrow the bounds making combustion less likely. These calculations discount the effects of moisture on the burning and assume that the propane ignition characteristics are representative of the mixture of organic species pyrolyzed from the wood and released from incomplete burning of wood. Neither assumption is entirely valid, but the results are indicative of the combustion limitations involved.

COMMERCIAL HIGH TURBULENCE BURNER

A residential wood burning appliance has been developed under a DOE contract by Professor Hill at University of Maine. The burner demonstrates that increased efficiencies can be obtained with an improved design of the combustion and heat recovery system. The burner is a residential boiler (water heater) for a central heating system that incorporates several factors beneficial in controlling air pollution emissions. The combustion is supported by both forced draft of combustion air and induced draft of flue gases, such that a high turbulence level can be maintained in the burning areas, yet not develop a firebox pressure exceeding ambient. It operates only at a fixed, relatively high burning rate ($\sim 150,000$ Btu/hr) comparable to one of the large radiant heaters. Several characteristics of this design favor low organic and CO emissions:



$$\text{Inert Ratio} = \frac{\text{Inert Fraction}}{\text{Active Fraction}} = \frac{N_2 + CO_2/0.53}{CO + Air + C_3H_8}$$

N_2 in the inert fraction is the nitrogen in excess of that corresponding to the oxygen in the air in the active fraction

The air, CO, and C_3H_8 are plotted as volumetric percents of their sum in the total gas stream. This sum is considered to be the active fraction. The inert fraction contains CO_2 and the N_2 in excess of that associated with the air in the active fraction at room temperature.

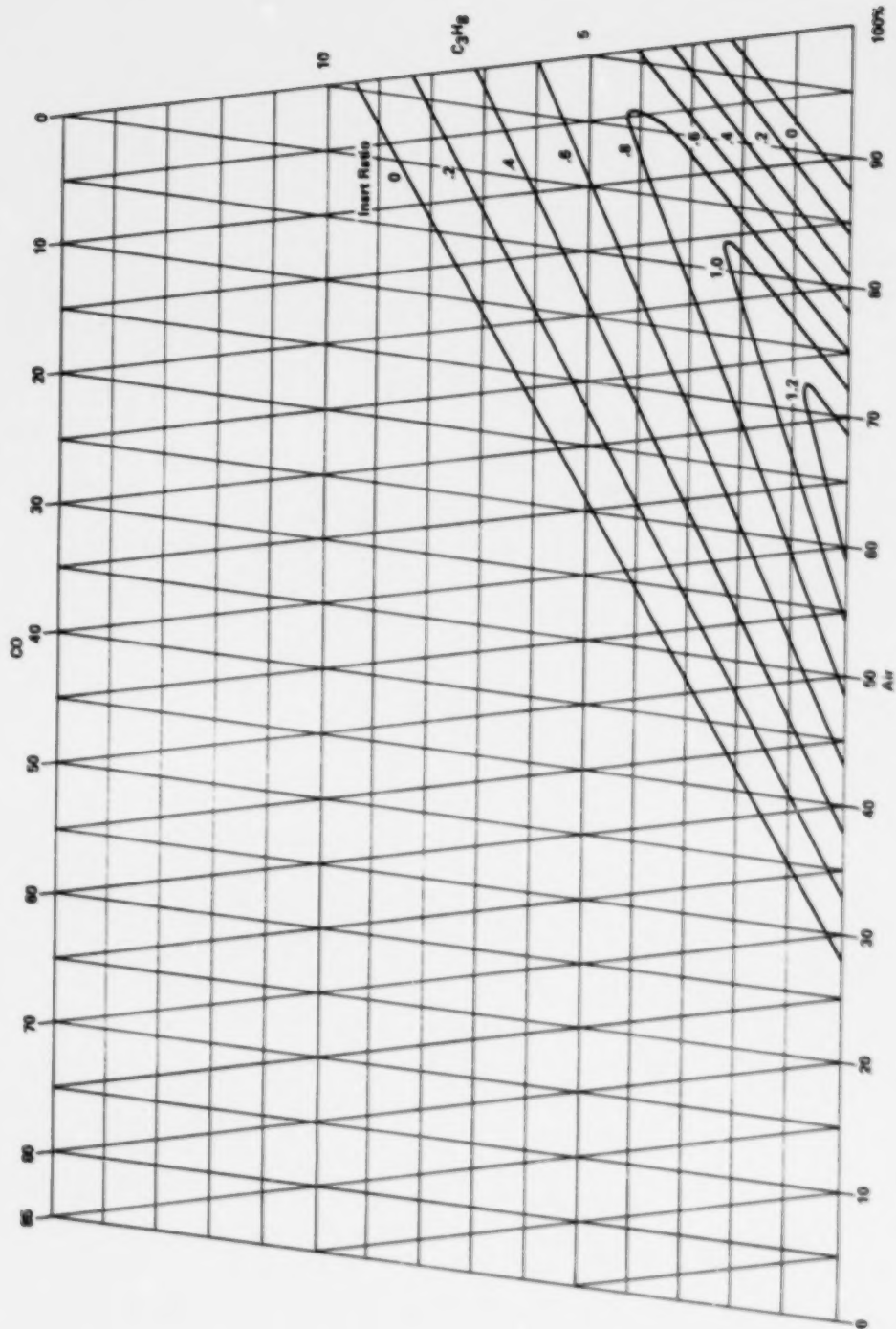
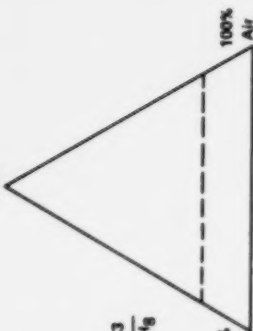


FIGURE 3. LIMITS OF IGNITION AT 20°C.

100%
C₃H₈



$$\text{Inert Ratio} = \frac{\text{Inert Fraction}}{\text{Active Fraction}} = \frac{N_2 + CO_2/0.53}{CO + Air + C_3H_8}$$

N₂ in the inert fraction is the nitrogen in excess of that corresponding to the oxygen in the air in the active fraction

The air, CO, and C₃H₈ are plotted as volumetric percents of their sum in the total gas stream. This sum is considered to be the active fraction. The inert fraction contains CO₂ and the N₂ in excess of that associated with the air in the active fraction at room temperature.

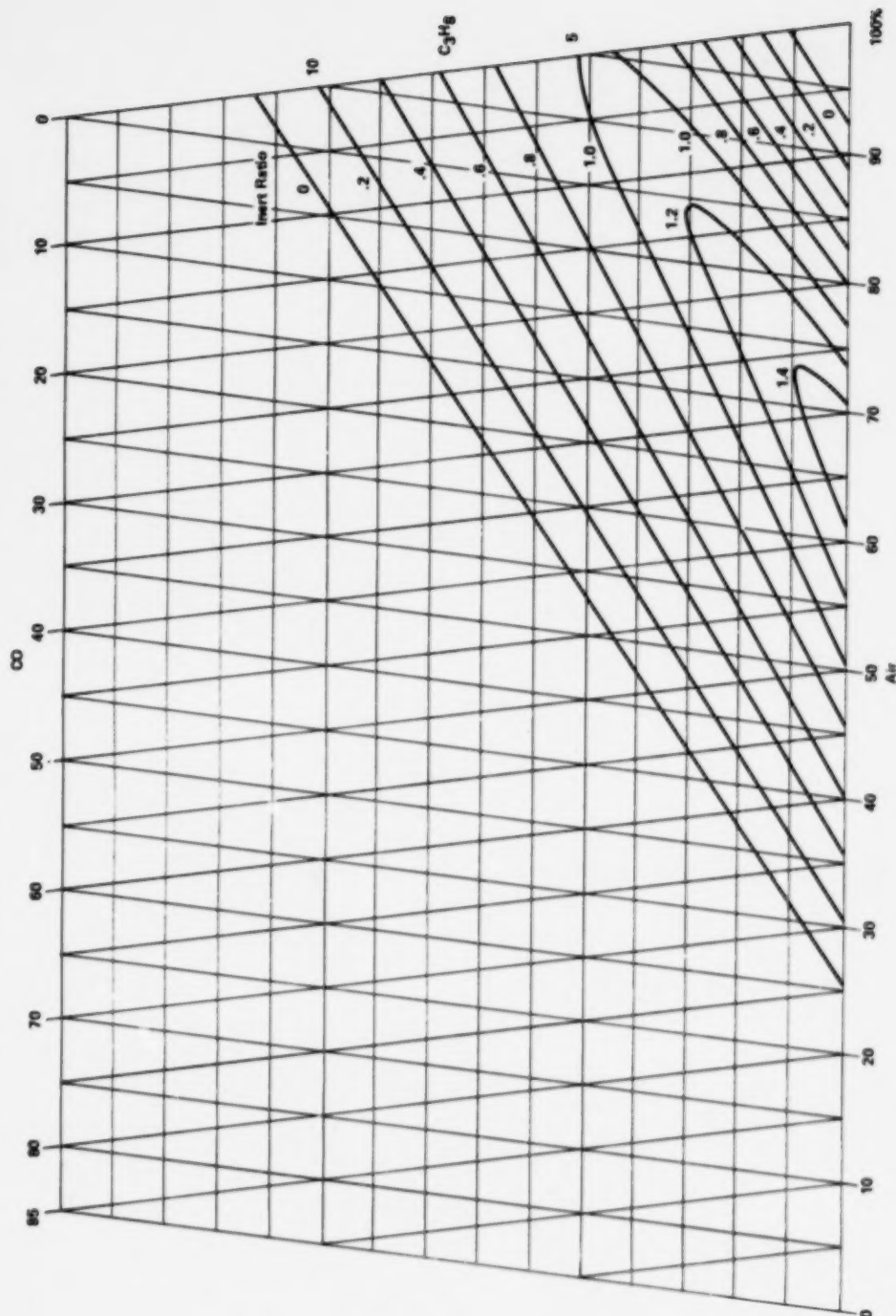
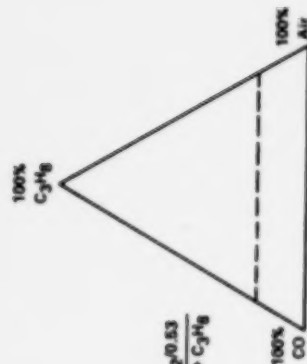


FIGURE 4. LIMITS OF IGNITION AT 270°C.



$$\text{Inert Ratio} = \frac{\text{Inert Fraction}}{\text{Active Fraction}} = \frac{N_2 + CO_2 \cdot 0.53}{CO + Air + C_3H_8}$$

N_2 in the inert fraction is the nitrogen in excess of that corresponding to the oxygen in the air in the active fraction

The air, CO, and C_3H_8 are plotted as volumetric percents of their sum in the total gas stream. This sum is considered to be the active fraction. The inert fraction contains CO_2 and the N_2 in excess of that associated with the air in the active fraction at room temperature.

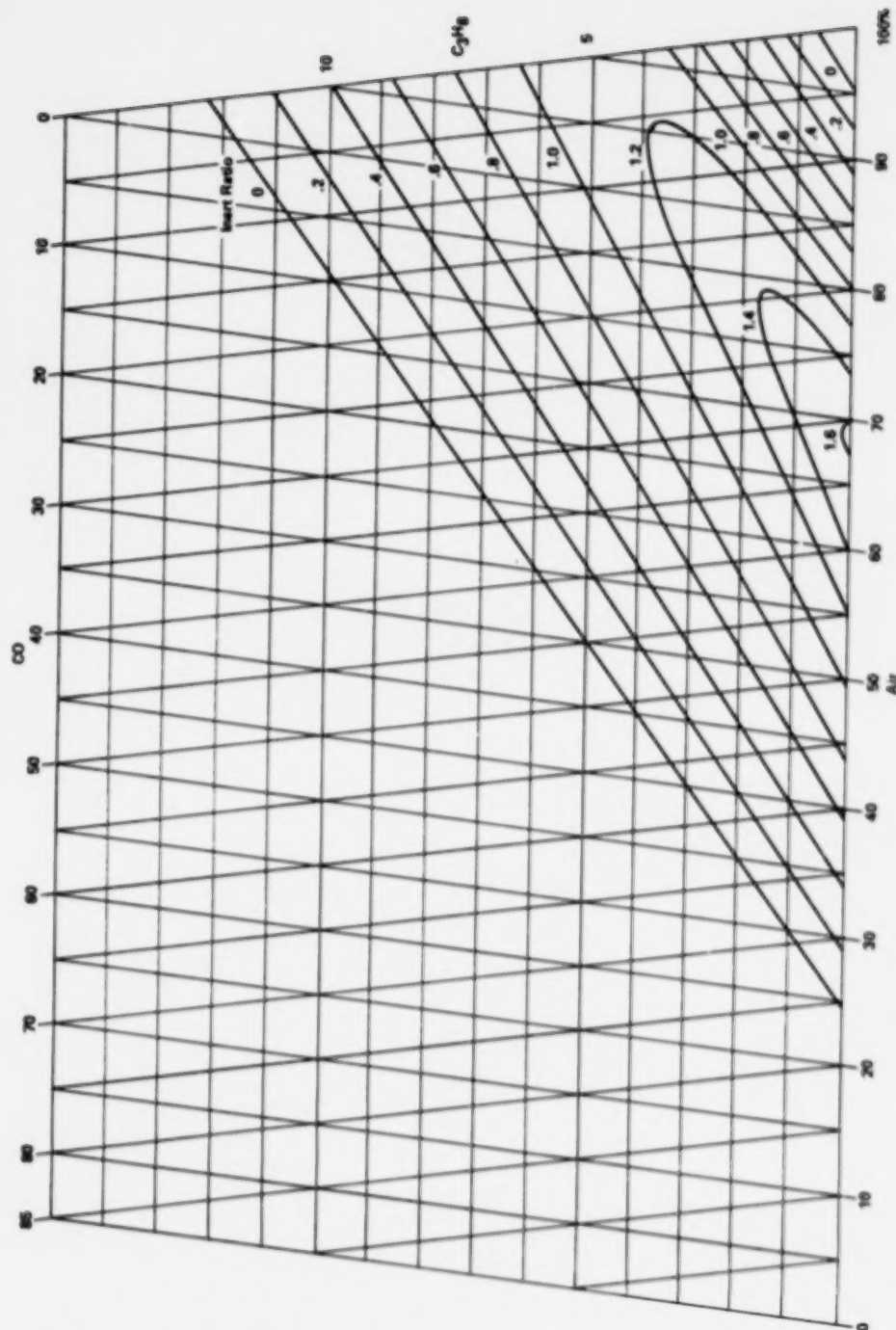
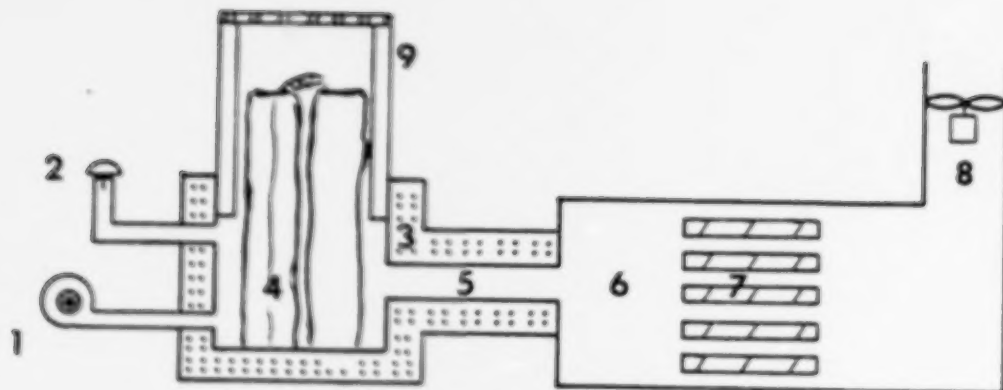


FIGURE 5. LIMITS OF IGNITION AT 520°C.

- High turbulence level in primary burning area
- Primary combustion products isolated from inventory of wood
- Inventory of wood cooled by water-jacketed chamber
- Burning confined to small portion of the wood inventory
- Refractory lined primary combustion area
- Refractory lined secondary combustion area
- Large pieces of wood utilized to reduce excessive pyrolysis early during burning cycle
- Burning restricted to high rates, with heat storage provisions to accommodate lower heating requirements.

Figure 6 shows a schematic sketch of the furnace, showing the principle components. A commercial production version (Dumont) of this wood burner was obtained for operation and analysis in the laboratory.



- | | |
|-----------------------|----------------------------------|
| 1 - forced draft fan | 6 - low velocity ash chamber |
| 2 - secondary air | 7 - fire tube heat exchanger |
| 3 - refractory base | 8 - induced draft fan |
| 4 - stacked wood | 9 - water jacket for wood charge |
| 5 - refractory tunnel | |

FIGURE 6. WOOD FIRED RESIDENTIAL BOILER
UTILIZING HIGH TURBULENCE BURNING.

SECTION 6

EXPERIMENTAL PROGRAM

LABORATORY FACILITY

The test facility assembled at Battelle for this program consists of three test sites, each with an independent, prefabricated, insulated chimney exhausting within a high bay area in the building. Thus, the chimney effects on draft are not affected either by outside wind or by the building's transient pressure fluctuations. Radiant stoves are mounted on electronic scales, such that total weight losses associated with fuel burning are continuously monitored. Figure 7 shows the facility arrangement and dimensions of a one stove and stack system.

The gases being continuously monitored are CO, CO₂, NO, O₂, SO₂, and total hydrocarbons (THC). The O₂ analyzer is a Taylor Servomex Type OA272 paramagnetic analyzer, the THC analyzer is a Beckman Model 402 high-temperature flame ionization detector analyzer. The CO₂, CO, and NO analyzers are Beckman nondispersive infrared analyzers. The SO₂ is measured by an electrochemical analyzer. The THC instrument provides a continuous indication of organic content in the flue gas. Because the specific composition of these organic species is constantly changing, a definitive calibration of the instrument for actual flue gas is not possible, although calibrated using methane, the instrument reading is interpreted as a semi quantitative measurement of all organics. All instrumentation is kept in a positive air pressure room where the air is supplied through an activated charcoal filter. The room is kept closed and is cooled by two air conditioning units.

The permanent gas sampling system pulls the flue gases from the stack at the point where the hot combustion products leaving the stove enter the stack. There is a 5/8" tube probe that extends the entire diameter of the stack. This probe is filled with pyrex wool and has two rows of 1/8"

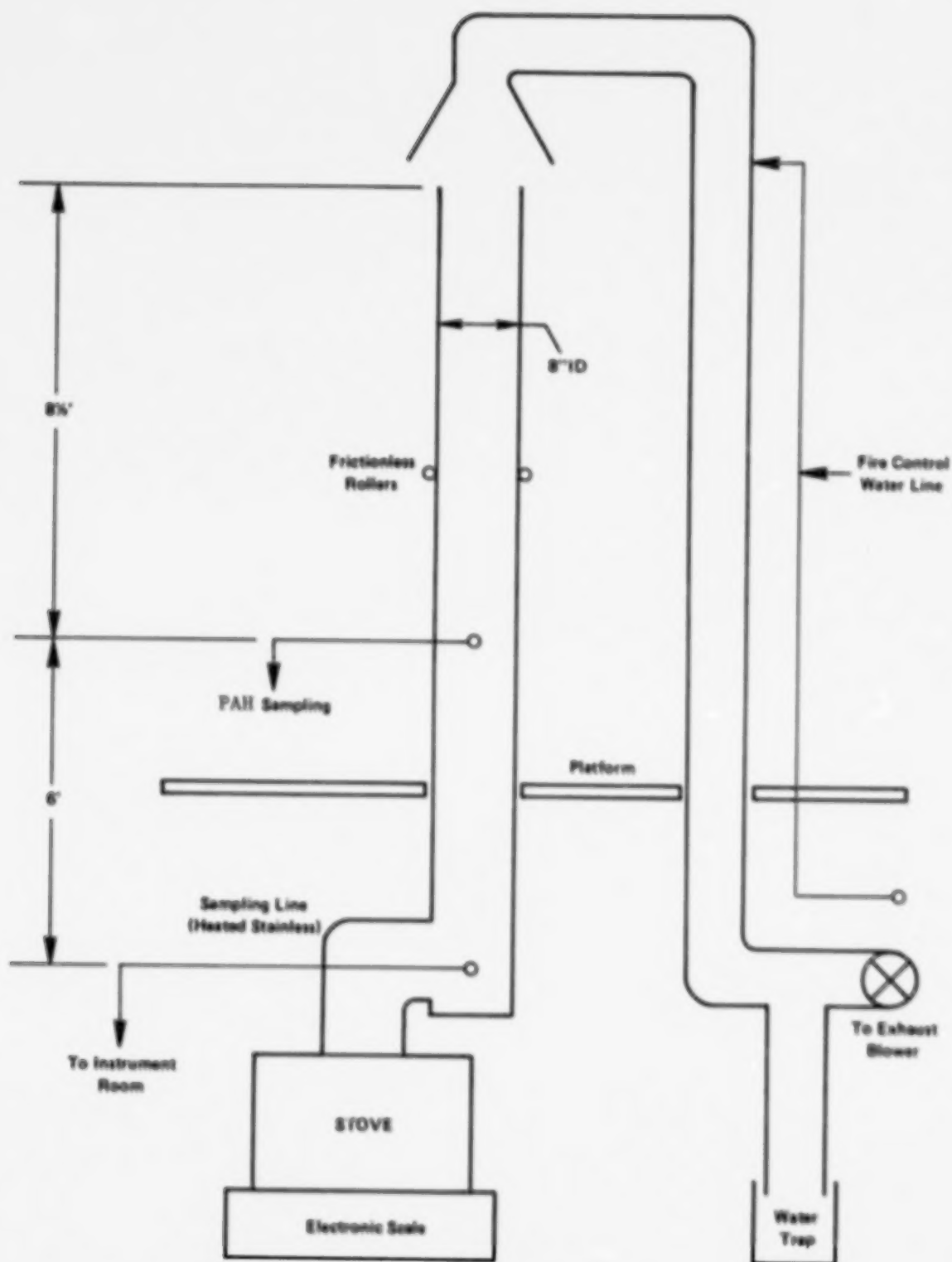


FIGURE 7. LABORATORY INSTALLATION OF STOVE WITH STACK AND VENT SYSTEM.

holes the length of the probe. After the gases are filtered in the probe they are pumped through a short heated flexible teflon line to a longer heated stainless steel line to the control room. The gases then pass through a Teflon bellows pump, after which the gas stream is split. Part of the sample stream is sent directly to the TMC analyzer, the rest is passed through a cold trap and cold filter to remove excessive water vapor and heavy organic vapors before entering the other analyzers. Figure 8 shows a schematic diagram of this system.

OPERATING PROCEDURES

In preparation for a run, the gas sampling lines are flushed with acetone to remove oils and tars from the sample lines. The pump is also cleaned. The gas sampling probe is removed from the stack and the glass wool replaced. The cold traps are cleaned and then placed into operation. The instruments are purged with nitrogen and spanned with appropriate span gases. Any adjustments to the instruments are done at this time. Once the sampling system and the instrumentation is working correctly, a charge of kindling is placed in the stove and ignited. The kindling burn heats the stove and generates a bed of hot coals. When 80 percent of the scrap wood is consumed the pretest burn is started by charging the desired quantity of wood. The pretest burn is used to assure the stove is operating at the desired conditions. As soon as 90 percent of the pretest wood is burned the actual test is started while not changing any conditions of the stove. In unusual cases not requiring hot starts the pretest at the identical operating conditions is omitted. A test run consists of the burning of a given charge of wood in a batch process immediately following the pretest burn. The test run lasts until 95 percent of the added wood is lost as measured by the scale.

At the end of the day, the sampling system is turned off and nitrogen is passed through all the instruments to recheck their zero and remove combustion gases from the instruments.

EMISSION MEASUREMENTS

During all tests the millivolt signals from the instruments are recorded on strip chart recorders and once every minute a Doric Digitrend

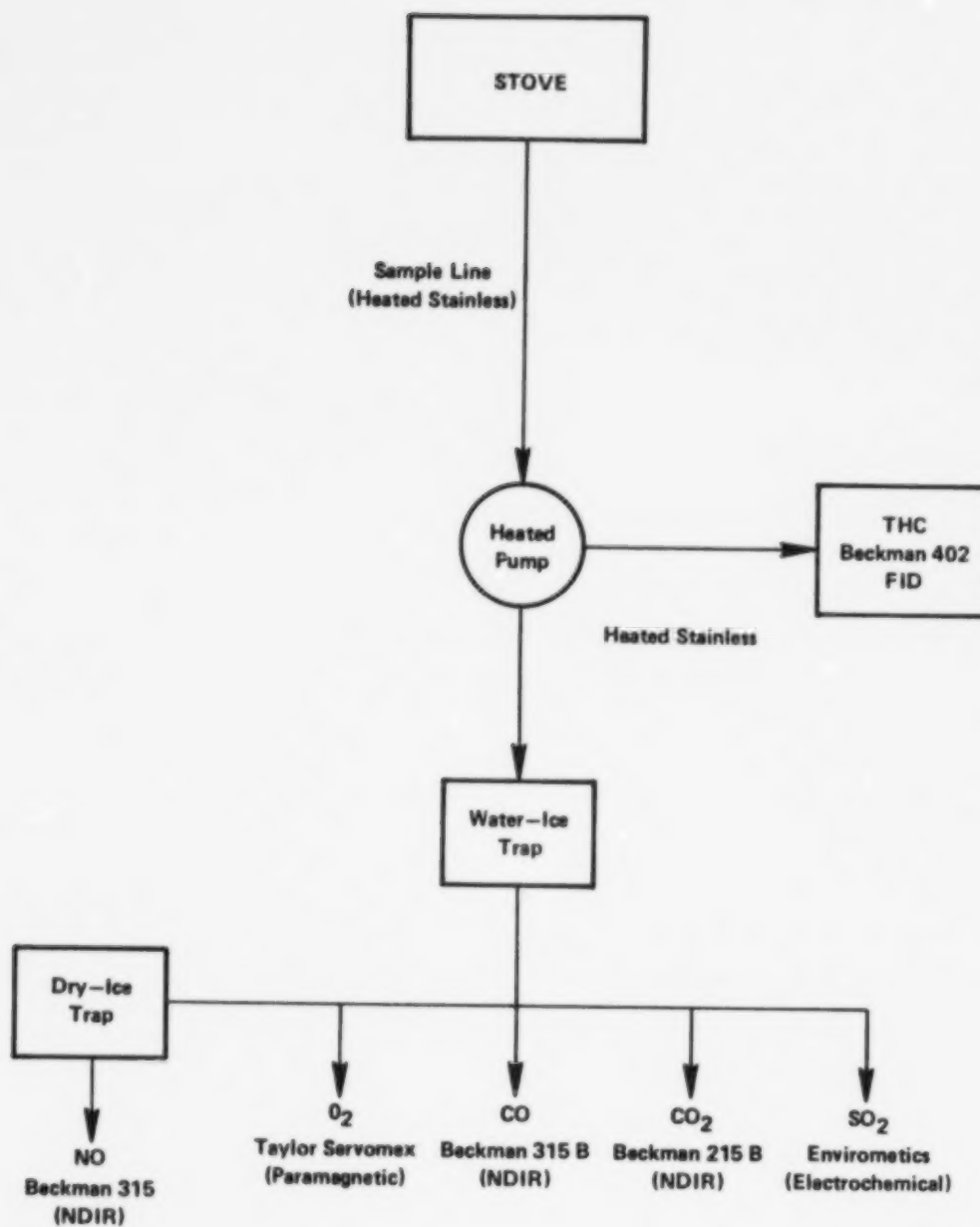


FIGURE 8. CONTINUOUS GAS SAMPLING SYSTEM.

220 Datalogger scans the data from the gas analyzers and the thermocouples in the stove. The Datalogger prints this information and also records it on a cassette tape by a data link with a Tecktran 815 data cassette recorder. Notes are taken manually during the runs such as the amount of wood, type of wood, stove operating conditions, the time of start and end of test, and other observations. Also a log sheet of data is taken at intervals during operation in case the Datalogger goes down, and it also shows trends during the test.

PAH MEASUREMENTS

During some test runs, the flue gas is sampled to determine the concentration of PAH. Figure 9 shows the sampling equipment used: a modified EPA Method 5 apparatus. This allows the collection of particulate emissions using filtration, followed by collection of the gas phase material by adsorption on the XAD-2 resin. The sampling rate is maintained constant at about 20 l/min (~ 0.75 cfm) during the entire sampling period with the probe inlet at the stack center. The sampling probe inlet velocities have been appreciably higher than stack gas velocities. However, the effects of non-isokinetic sampling are considered insignificant because of the small particle sizes. Using an electric aerosol analyzer, the mass median diameters of suspended particles were measured as 0.22 and 0.39 at the PAH sampling location during two runs in this facility. Fuchs (19) has shown that for particles smaller than 5 μ m, excessive sample withdrawal velocities result in collection efficiencies still above 95 percent because the smaller particles follow the gas stream lines.

Following sample collection, the organic materials are extracted from the column and probe system and analyzed for PAH compounds. The probe wash and extract from the filter are combined into one sample for analysis, and the column extract constitutes a second sample. Although the sample collected on the probe walls and the filter can be defined as particulate, it must be recognized that they consist essentially of condensed organic species. The distribution between gaseous organics as retained by the XAD-2, and particulate organics caught on the filter, must be recognized as depending primarily on the temperature of the stream at the point of collection on the filter and walls. Appendix B presents details of the PAH analysis procedures.

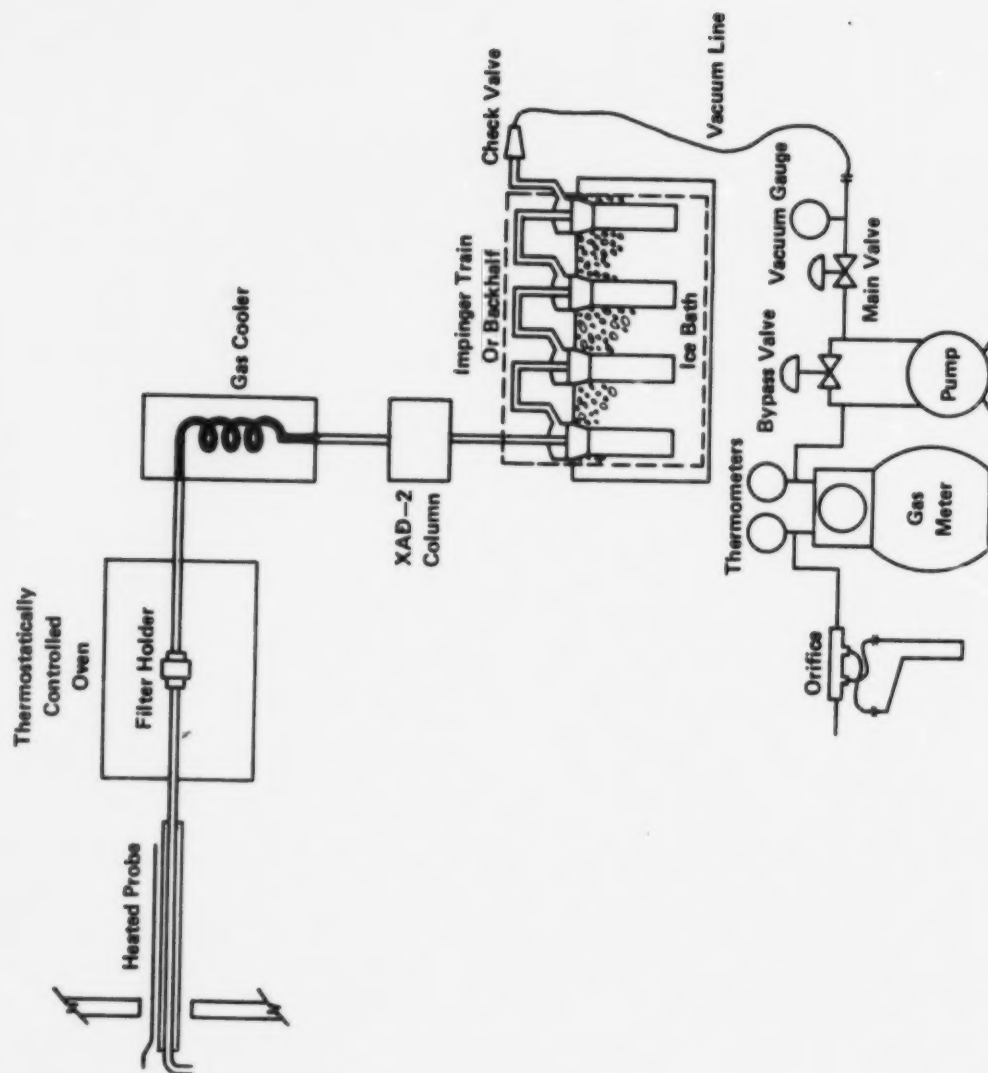


FIGURE 9. PARTICULATE AND PAH SAMPLING SYSTEM.

DATA PROCESSING

After each day of testing, taped raw data from on-line gas composition instruments and the scale weight are calculated and ultimately read out as volume fraction of the flue gas at each minute of burn, and weight of wood remaining unburned at each minute. These one-minute recordings are subsequently machine averaged for the entire test run, and this average reported as the time-averaged gas composition for that run. The emissions have thus not been normalized to an arbitrary flue gas O_2 and moisture content, such as 3 percent dry. Such a normalization would in all cases increase the numerical pollution concentration. These time averages are then manually converted to emission per weight of wood burned using a calculated weight flow of flue gas for the entire run and the weight of wood burned as measured by the platform scale. The volumetric composition of the flue gas is also machined plotted against time, such that trends, anomalies, and relative values can be easily identified. The calculated emissions provide the basis for evaluating the effects of imposed variables on total emissions for a test, and the flue gas composition plots provide a basis for diagnosis of the phenomena occurring and demonstrate the real-time effects of changes imposed on a stove during operation.

FUEL WOOD USED

Four types of wood fuel have been used, as follows:

- White oak cordwood, air dried, 20.7 percent moisture. Normally split and round pieces were fired together.
- Pine cordwood, not air dried (i.e., green), 42 percent moisture. Normally split and round pieces were fired together.
- Douglas fir brands 3/4 inch on 1 inch centers, oven dried, null moisture.
- Oak lumber, nominal 4 inch x 4 inch, cut diagonally into triangular pieces, thoroughly air dried, 12.4 percent moisture. These 4 x 4s were fired only in this form, with all surfaces sawed.

The moisture contents of the oak and pine were determined by weight loss upon storage in a 100+°C oven for 48 hours, and is stated on the wet basis.

SECTION 7

EXPERIMENTAL PROGRAM OBSERVATIONS

Table 2 lists the averaged flue gas compositions and emissions obtained during this program. The burning rate, fuel, and burning mode have been identified for each test run. The gas compositions which are mechanically recorded each minute are machine plotted, and several representative plots are reproduced in Appendix B. Notes have been added to identify the burning phenomena occurring at each time. All tests of the radiant stoves were started when a charge of wood was inserted into hot stove with a bed of burning embers. The high turbulence burner was started cold in each test. These averaged data are presented only for tests during which no changes were imposed on the stove operation or controls.*

The combustion in wood stoves, and the resulting emissions, can be modified in many ways. In this experimental program several modifications were made in stove operation in attempts to correlate specific changes in emission factors with a specific combustion modification. Synergistic effects of several simultaneous modifications were not specifically sought. However, each set of tests conducted to demonstrate the effects of a specific modification necessarily depends on the stove design and operating parameters in use at the time. The effects of a specific modification under different design and operating conditions can only be assumed, and the synergistic effects determined by inference.

The modifications conducted in this laboratory program were of three types; stove design, fuel properties, and operator techniques. The uses of non-wood fuel and combustion additives were not considered. The use of processed wood, such as pellets, was also not considered, as this fuel can most effectively be burned in equipment specifically designed for its use.

* A group of 32 test runs was also conducted for TVA in a similar manner and the detailed results of these tests will be separately reported by that agency, including overall thermal efficiency calculations.

TABLE 2. EMISSIONS AND OPERATING CONDITIONS

Test Run Number	Wood Species	Piece Shape	Burning Rate lb/hr	Fuel Burned lb/test	Time Averaged Gas Composition, as measured					
					Percent by Volume			Parts Per Million		
					CO	CO ₂	O ₂	THC	NO	SO ₂
Up Draft Burning Mode with Grate (Modified Rite-way)										
77	Oak	Split	14.4	25.3	2.5	11.0	9.1	6700	110	60
78	Oak	Split	31.8	33.9	2.3	10.9	9.3	6400	80	50
91a	Oak	4 x 4	16.5	21.0	3.6	13.8	6.8	7100	120	50
92	Pine	Split	20.7	18.2	3.9	15.3	5.6	9100	180	70
93	Pine	Split	21.6	30.3	2.0	13.3	8.2	7100	100	50
94	Oak	4 x 4	20.9	24.0	2.7	10.6	9.2	5900	90	40
95	Oak	4 x 4	27.1	25.8	5.4	13.0	6.1	9900	130	50
Up Draft Burning Mode with Hearth (Defiant)										
18	Oak	4 x 4	5.8	6.3	0.1	1.9	19.6	1800	40	20
19	Oak	4 x 4	14.4	10.2	0.2	5.9	15.4	1600	80	20
20	Oak	4 x 4	19.5	14.4	0.3	8.5	12.2	1100	120	10
Side Draft Burning Mode (Defiant)										
37	Oak	4 x 4	6.3	5.9	1.8	6.2	15.1	8300	100	40
36	Oak	4 x 4	11.8	9.8	0.6	10.1	10.7	1900	50	20
34	Oak	4 x 4	17.4	12.9	1.2	11.9	8.1	2800	80	20
35	Oak	4 x 4	19.2	41.9	2.5	11.7	7.8	5300	90	40
38	Oak	4 x 4	12.3	26.4	1.8	9.6	11.1	7600	120	60
82	Oak	Split	16.7	24.0	0.5	10.1	10.6	1800	90	10
83	Oak	4 x 4	18.7	23.4	2.5	13.0	6.6	6200	80	30
84	Pine	Split	18.4	26.1	0.5	8.6	11.9	1800	70	10
85	Oak	Split	16.5	15.2	0.5	13.0	9.4	1200	110	10
86	Oak	Split	13.0	15.0	1.5	12.5	9.7	3400	90	20
87	Oak	Split	16.6	14.9	1.1	12.9	9.4	2400	80	20
88	Oak	Split	15.6	14.6	0.9	13.9	8.5	1100	50	10
89	Oak	Split	14.6	14.6	0.4	13.8	8.8	400	50	10
90	Oak	Split	15.0	15.5	0.8	12.5	9.9	800	60	10
High Turbulence Burner (Dumont)										
51	Oak	Split	21.9	37.3	0.3	9.6	10.9	300	140	<10
52	Oak	Split	22.1	35.9	0.6	6.2	14.2	2000	70	20
53	Fir	Split	20.9	21.6	1.6	8.3	11.2	1900	50	40
91	Oak	Split	24.1	39.3	0.1	2.1	18.9	200	20	10
Down Draft Burning Mode (Modified Defiant)										
42	Oak	Split	7.3	13.6	0.2	3.4	17.5	3100	70	60
43	Oak	Split	10.3	16.2	0.2	3.4	17.6	3100	80	60
60	Oak	4 x 4	18.4	15.4	0.5	9.4	11.3	1000	80	20
61	Oak	Split	19.1	16.2	1.0	8.7	11.6	1600	210	20
63	Oak	Split	12.8	15.8	0.1	5.4	15.5	600	110	10
64	Oak	Split	11.3	14.9	0.3	4.9	15.8	900	50	10
80	Oak	4 x 4	13.7	16.2	0.4	7.4	13.2	600	40	10
81	Oak	Split	20.4	25.5	0.1	8.5	12.3	200	90	<10
65	Fir	Split	10.7	15.0	0.4	6.3	14.3	900	30	10
70	Fir	Split	18.0	16.8	0.4	6.9	13.9	2000	40	20
71	Oak	Split	9.8	14.7	0.1	2.5	18.7	1500	20	10
76	C	Split	8.0	8.0	+	7.5	13.4	100	60	<10
46	Fir	Split	14.0	14.0	0.3	5.0	15.8	1100	20	<10
47	Oak	Split	13.2	23.8	0.3	5.9	15.1	3200	80	10
48	Oak	Split	15.6	23.5	0.3	6.0	14.9	1000	220	10
49	Fir	Split	14.5	12.0	0.4	8.1	12.6	600	130	10
50	Pine	Split	10.1	12.4	0.1	2.3	18.9	1200	100	20
Down Draft Burning Mode - Heated Air Supply (Modified Defiant)										
68	Oak	Split	15.1	13.4	0.2	8.3	12.3	300	260	<10
69	Oak	Split	16.0	12.0	0.2	9.9	10.6	200	220	<10
72	Oak	Split	21.6	15.8	0.1	7.0	13.9	1300	70	10
73	Fir	Split	24.6	9.0	0.7	12.2	8.0	1600	80	20
Down Draft Burning Mode, Reduced Area and Insulated Bed (Modified Defiant)										
66	Oak	Split	12.9	13.8	0.1	4.5	14.4	900	70	<10
67	Oak	Split	13.0	14.6	0.0	5.3	15.4	800	200	<10

TABLE 2. (Continued)

Test Run Number	Excess Air, percent	Stack Temp. of	Emissions			Comments
			lb/1000 lb Wood	lb Wood	NO	
Up Draft Burning Mode with Grate						
77	80	710	34	220	1.1	Small pieces
78	80	720	33	200	0.8	Small pieces
91a	40	950	32	280	1.0	PAH sample
92	30	970	44	330	1.6	Oven dried wood
93	70	760	25	120	0.7	Green Pine
94	80	990	34	270	1.0	
95	30	960	42	400	1.0	
Up Draft Burning Mode with Hearth						
18	2050	560	113	90	4.9	Low rate
19	290	760	19	33	2.0	Medium rate
20	140	1060	8	37	1.7	High rate
Side Draft Burning Mode						
37	340	270	112	420	2.6	Low rate
36	110	580	12	63	0.6	Medium rate
34	60	680	15	100	0.8	High rate
35	60	660	26	220	0.8	Large load
38	120	450	53	210	1.6	Thermostat control
82	110	620	10	50	0.9	All split wood
83	40	700	28	190	0.6	PAH sample
84	130	590	9	40	0.6	PAH sample, all split
85	90	640	6	44	1.1	
86	90	630	18	140	0.9	
87	80	620	13	100	0.2	
88	70	700	5	75	0.1	
80	80	670	2	34	0.1	
90	100	620	4	74	0.1	
High Turbulence Burner						
51	110	330	2	30	1.6	Many small pieces
52	220	250	18	97	1.2	4 large pieces, 1 unburned
53	120	290	16	222	0.8	Brands only
91	920	340	5	25	1.2	Large pieces, normal run
Down Draft Burning Mode						
42	560	340	56	67	2.5	Low burn rate
43	560	370	56	64	2.7	Medium burn rate
60	120	800	7	61	1.0	Saved 4x4
61	130	770	10	110	2.5	Small split pieces
63	290	610	7	19	2.2	4" round wood
64	330	570	11	48	1.1	Medium splits
80	180	710	5	59	0.6	PAH sample
81	140	740	2	6	1.1	Frequent additions
65	220	640	9	74	0.6	14% moisture
70	200	660	16	49	0.6	28% moisture
71	880	410	34	39	0.9	31% moisture
76	180	720	1	3	2.0	Charcoal fuel
46	320	620	16	67	0.6	Secondary air varied
47	280	510	33	54	1.6	Normal bed area
48	250	500	10	44	3.8	Reduced bed area
49	150	600	5	60	2.3	Reduced bed area
50	1000	330	26	28	4.1	Reduced bed area
Down Draft Burning Mode - Heated Air						
68	140	630	2	20	3.3	370 F primary air
69	100	680	1	15	2.3	370 F primary air
72	200	600	11	19	1.1	440 F secondary air
73	61	980	10	71	0.8	440 F secondary air
Down Draft Burning Mode, Reduced Area and Insulated Bed						
66	380	540	11	25	1.6	Bed channeling
67	280	600	8	4	3.9	No bed channeling

The following paragraphs describe various modifications investigated with the observed effects on emissions. For some modifications the emission factors resulting from complete tests are presented, and in some modifications, visual and instantaneous results are more appropriate.

This section is a discussion of stove combustion modifications. In each case the objective or basis of the modification is presented, followed by experimental technique, observed results, and appraisal of the results.

The very significant effects of burning rate on flue gas composition and emissions must be considered in any comparison between stoves or between the same stove in different tests. These effects will be discussed later in this section. Most of the data reported here are from tests conducted at medium and high rates for the size of stoves used. The two basic radiant stoves modified and used in this study have manufacturers nominal ratings of approximately 13 pounds wood per hour, assuming 20 percent moisture in the wood and 60 percent overall thermal efficiency. The test program included operation at burning rates both greater and smaller than these nominal ratings. Sustained burning at hold-fire conditions (closed dampers) would naturally be much below these burning rates.

STOVE DESIGN FACTORS

An operator has little control of the design of the stove except at the time of stove purchase. At that time the operator decides which type and design to buy, depending on personal preference and the designs that are available. Some stoves however, have limited capabilities to operate in different modes, such as by use of an internal damper.

Air Flow Path in Stove

Three of the four generic designs of air flow path were incorporated into one stove (Defiant) for a direct comparison of emissions. The up-draft mode with the hearth was achieved by opening the damper thus

permitting the primary combustion products and pyrolysis products to pass directly upward and out of the stove. In the side draft mode all primary combustion products passed under the side arch or baffle, and through the more extensive internal passages before leaving the stove. In both of these modes the fire rested on an impervious hearth and primary air was supplied through tuyeres at the hearth level. The Defiant was also modified to burn in the down draft mode as shown in Figure 10. In this mode the fire bed was entirely supported on a grate, with the bed area reduced by about one third by a retaining firewall composed of bricks. The primary combustion products passed downward through the grate, under the arch, and then through the same passages as used in the side flow design. In this mode, the primary air was supplied through an opening in the end door.

The up-draft mode with the grate was obtained in another stove (Riteway) modified to provide all air supply upward through the grate and leaving the top of the combustion chamber.

The results of the tests are shown in Table 3. As can be seen from the data, there is no large difference between the three modes of operation of one stove. Both gas composition and emissions are shown for the three different modes of burning for various burning rates. The down-draft mode at high burning rates is consistently low in THC emissions. When the burning rate is low the thermal buoyancy forces result in a local updraft flow (countercurrent) within parts of the bed, overcoming the overall average down flow through the bed. This results in channeling and flow recirculation within the bed, and rapid pyrolysis of wood throughout the bed. Extensive pyrolysis products can thus be released into the counter stream and ultimately pass with the channelled down flow out of the bed without burning. The effects of bed channeling on the CO and the emissions is also evident when comparing tests 66 and 67 (see Table 2). Using several windows in the stove permitted observations of gas flow through the bed. In test 66 extensive counterflow and channeling were observed, whereas in test 67 uniform downflow throughout the bed was maintained.

The up draft burning mode using the grate produced higher THC and CO emissions than the other modes at comparable burning rates, although the PAH emissions do not support this trend.

TABLE 3. EMISSIONS FROM DIFFERENT MODES OF
BURNING FUEL: Oak 4 x 4

Test Run Number	Gas Composition		Emissions			Excess Air, percent	Burning Rate, lb/hr
	THC, ppm	CO, percent	1b/1000 lb wood PAH	THC	CO		
Side Draft Mode (Defiant)							
37	8300	1.8	ND	112	420	340	6.3
36	1900	0.6	ND	12	63	110	11.8
34	2800	1.2	ND	15	100	60	17.4
83	6200	2.5	0.035	28	190	40	18.7
84	1800	0.5	0.045	9	40	130	18.4**
Down Draft Mode (Defiant)							
42	3100	0.2	ND	56	67	560	7.3*
67	800	0.0	ND	8	4	280	13.0
80	600	0.4	0.050	5	59	180	13.7
60	1000	0.5	ND	7	61	120	18.4
Up Draft Mode with Hearth (Defiant)							
18	1800	0.1	ND	113	90	2050	5.8
19	1600	0.2	ND	19	33	290	14.4
20	1100	0.3	ND	8	37	140	19.5
Up Draft Mode with Grate (Riteway)							
77	6700	2.5	ND	34	220	80	14.4*
91a	7100	3.6	0.018	32	280	40	16.5
94	5900	2.7	ND	34	170	80	20.9
95	9900	5.4	ND	42	400	30	27.1
78	6400	2.3	ND	33	200	80	31.8*
High Turbulence (Dumont)							
91	200	0.1	0.011	5	25	920	24.1*
51	300	0.3	ND	2	30	110	21.9*

* = Oak Logs

** = Green Pine

ND = Not determined

Gas Flow Sequence in Down Draft Mode

1. Primary air enters through door at left side
2. Rises to go over top of brick firewall staying in front of the closed bypass damper.
3. Descends on the right of the firewall, passing first downward through the inventory of unburned wood.
4. Continues descent downward through the burning wood.
5. Continues downward through the grate.
6. Passes horizontally under the baffle into the secondary combustion chamber.
7. Mixes with secondary air as it rises through the secondary combustion chamber.
8. Passes behind the closed bypass damper to rear center of stove
9. Passes upward through top rear of stove into fluepipe.

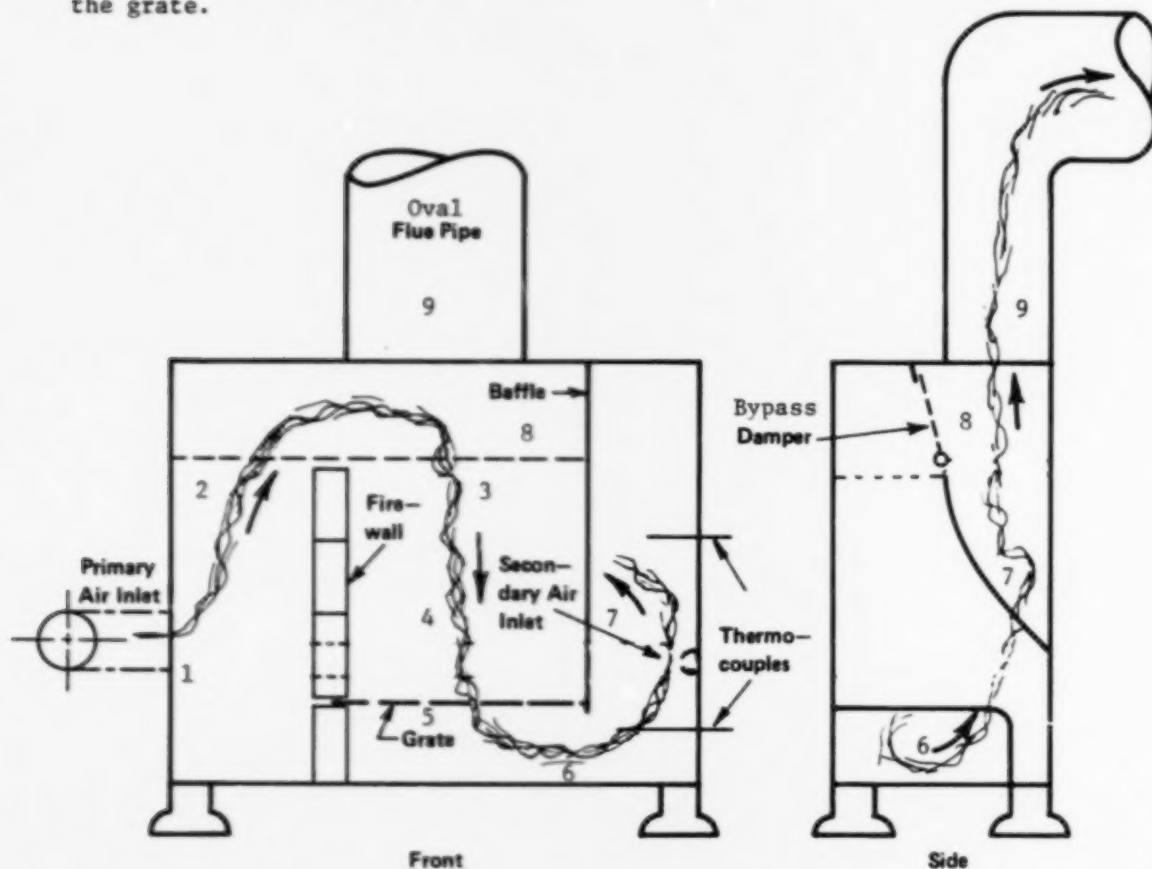


FIGURE 10. CONFIGURATION OF STOVE CONVERTED TO DOWN DRAFT MODE.

The Dumont high turbulence burner produced lower emissions than the up draft or side draft modes when burning oak fuel. The emissions were comparable to the lowest values obtained with good down draft burning, as obtained in test 67.

Primary Air Preheat

One purpose of preheating the primary air is to increase the rate and completeness of the primary combustion of the wood. The combustion products will hopefully be more completely oxidized because the air entering the combustion zone is heated, thus raising the temperature of the reaction and thereby the reaction rate. The combustion products are also less cooled or quenched by the air supply.

Using a stove operating in the downdraft mode, tests were conducted in which the incoming primary air was preheated to 188°C (370°F). Air flow rate into the stove from a pressurized source was controlled so that the rate would be similar to other tests, i.e., 850 l/min (≈30 scfm). The preheating was done by passing the primary air through an electrically heated pipe and blowing this into the inlet of the stove. This arrangement is schematically shown in Figure 11. The heated air was the only primary air source of the stove, and used a large pipe in the stove's door side to reduce the air velocity and to distribute the air evenly in the stove. Oak logs, round and split, were used during these tests.

Even with the low emissions inherent with downdraft burning, reductions in emissions were obtained when the primary air was preheated with the outside source. The time averaged gas compositions from four entire tests were converted to emissions and are shown in Table 4. It is not certain if this effect would be observed to the same degree with other modes of burning, as the heated incoming primary air could promote early and extensive pyrolysis of the wood thus adversely affecting emissions. However, in downdraft burning these pyrolysis products cannot easily bypass the active burning area at the downstream edge of the bed, especially in the early stage, when there is a good bed of hot coals that the gases must pass through.

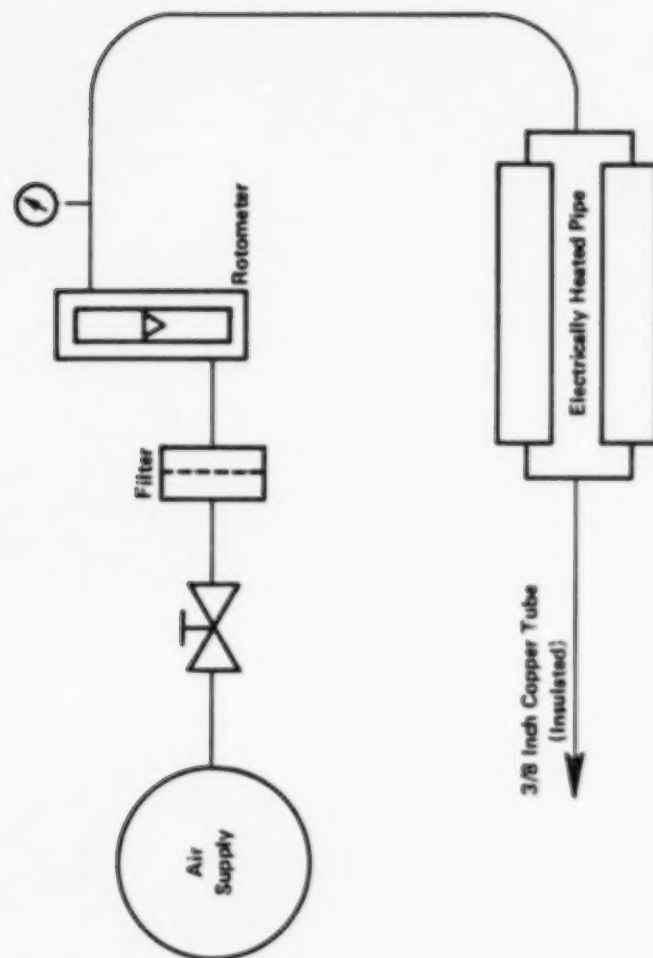


FIGURE 11. AIR PREHEAT SYSTEM.

TABLE 4. EFFECTS OF PREHEATED
PRIMARY AIR ON EMISSIONS

	Down Draft Burning of Oak Logs			
	Ambient Primary Air (80°F)		Heated Primary Air (370°F)	
Test Run Number	48	64	68	69
Burning Rate lb/hr	15.6	11.3	15.1	16.0
Gas composition as measured,				
CO, percent	0.3	0.3	0.2	0.2
THC, ppm	1000	900	300	200
Emissions, lb/1000 lb wood				
CO	44	48	20	15
THC	10	11	2	1

The preheating of primary air was thus shown to offer possibilities in reducing emissions in a wood burning stove. A main design problem to overcome is the location of the heat-transfer surfaces to preheat the air, while keeping the pressure losses low enough to prevent serious restrictions to the flow of air.

Secondary Air Preheat

Preheating of the secondary air is important to prevent cooling or quenching of the combustion products before leaving the stove so that secondary combustion can occur. An increase in the secondary air temperature broadens the flammability limits allowing initiation of secondary combustion.

The heating of the secondary air was accomplished by using the same preheater used for the primary air. The air supply temperature was 228°C (442°F) and the flow was controlled to about 2 l/sec (5 scfm). The heated air was introduced through the stove's own internal secondary air ducting before entering the secondary combustion chamber. This ducting provided inherent and additional heating of the secondary flow.

The preheating of the secondary air is assumed to have no effect on emissions unless secondary combustion has been established or can be initiated by the preheat. This is evident from a test burning wood which emitted large quantities of combustibles early in the burning cycle (dry fir brands). Secondary combustion started only when the heated secondary air was introduced into the stove. It is uncertain whether the preheat or just an increase of total air was the cause of secondary combustion. The secondary combustion was evident from the increased intensity of the flames in the secondary combustion chamber observed through a pyrex window.

The preheating of secondary air can achieve reductions in emissions by supporting secondary combustion, however, the achievement of secondary combustion is so strongly dependent on the gases present that the effect of preheating by itself is overshadowed.

Secondary Combustion

Secondary combustion is the combustion of the combustible materials not burned in the primary combustion or immediate vicinity of the wood. These materials can result from quenching of the primary combustion products or from pyrolysis of wood without burning downstream of the primary combustion region. This secondary combustion is achieved by mixing the gases from the wood and from the primary combustion with suitable oxygen at a temperature sufficient to ignite the mixture. In some stoves this is attempted directly above the burning wood and in other stoves the primary combustion zone is separated from the secondary combustion zone by a physical barrier, with the secondary air entering at a different location than the primary air. For secondary combustion to take place the gas composition must be within the flammability limits of the gases. Therefore the addition of secondary air could dilute the combustion gases to a fuel concentration below the flammability limit, or quench the mixture to below ignition temperatures.

The flammability limits calculated for CO and propane with air are shown in Figures 3, 4, and 5. Propane was chosen as being representative of wood pyrolysis gases realizing that the composition of the actual pyrolysis gases is extremely complex and varies during burning in actual cases. As can be seen from the triangular graph, the flammability region is very narrow and would explain the difficulty in obtaining and maintaining secondary combustion especially at low temperatures. The amount of inerts from completed combustion also affects the flammability as shown in Figures 3, 4, and 5 by making the range narrower. As the temperature of the combustion products increases, the flammability limits broaden, making secondary combustion easier to initiate.

The stove used for these observations has a separate secondary combustion zone. For the observation and determination of secondary combustion a pyrex window and a thermocouple were placed in the secondary combustion chamber. Different woods were burned so that different burning rates and emissions could be tested for secondary combustion. The tests were conducted in the downdraft mode permitting flames to persist the short distance from primary to secondary zones, but essentially precluding burning ember carry over. Secondary air was supplied through internal stove ducting which provided air preheat before mixing with the primary products.

During the test program there were very few occurrences of distinct secondary combustion when it was not being deliberately promoted. Even when secondary combustion was attempted, if and when it was obtained, it occurred only at high burning rates and for only a short period of time (less than five minutes). During one test the secondary air flow was intermittently stopped. With the secondary air inlet closed, emissions were high (CO: 2.3 percent, THC: 8200 ppm, and the oxygen: 3.6 percent). The inlet was then suddenly opened. One-minute data extracts from this test are shown in Table 5. When the secondary air inlet was opened an audible noise was heard, and the initiation of secondary combustion was indicated by the thermocouple located in the secondary combustion chamber. The initial pulse of secondary air was presumably heated above the equilibrium inlet temperature, as the supply duct was surrounded by the hot gas. Along with the indicated temperature increase of about 100°C (170°F), there was a decrease in emission levels. Later during that test when secondary combustion was still apparent, the secondary air inlet was suddenly closed. The results were a decrease in temperature in the secondary combustion zone and a sharp increase in emissions. Secondary combustion was not reobtained upon reopening of the air inlet after several additional minutes.

High temperature of the primary combustion products encourages secondary combustion by preventing quenching by the cold secondary air with primary products above 800°C (1500°F), large quantities of unheated secondary air still support secondary combustion. This was confirmed when a sight glass (2 1/2 inch diameter) in the secondary combustion chamber inlet was removed, permitting a large influx of room air. The associated initiation and maintenance of secondary combustion was very evident: CO concentrations dropped reversibly from 4 percent to below 1 percent, and THC concentrations dropped reversibly from 9000 ppm to about 1000 ppm as the window was opened and closed. However, these tests were run at very high burning rates to obtain the temperatures desired; the burning rates were over 20 pounds per hour. This is appreciably higher than a homeowner would normally operate a stove.

The concept of secondary combustion is very effective for the reduction of emissions. However, it is very difficult to attain when the stove is operated at lower burning rates more typical of consumer operation, where both the temperature and the turbulence level are lower.

Afterburning with Auxiliary Fuel

The purpose of an afterburner is to burn the emissions before they exit the stove. This is done by introducing fuel into the flue gas already containing sufficient air to burn the fuel and the combustible emissions. The fuel source could be external to the stove and could be a gas such as methane, propane or butane.

To observe the effects of an afterburner, a quarter inch stainless steel tube with 1/6 inch holes every inch was placed in the stove directly below the secondary air distributor tube while the stove was operating in the downdraft mode. Propane was used as the auxiliary fuel and was fed through a rotometer to monitor flow. The flowrate was from 2 to 3 cubic feet per minute into the secondary combustion chamber.

The introduction of propane directly into the secondary combustion chamber usually resulted in at least partial burning as indicated by gas temperature increases. Three example observations are cited in which at least some burning of propane occurred:

1. When the initial flue gas temperature was low (450°F, 230°C) and the oxygen content high (18.9 percent O₂), the introduction of propane increased the CO from 0.2 to 1.2 percent and the THC from 3100 to 7400 ppm. With this low initial temperature in the flue, the combustion of propane was evidently not completed as the gas left the stove, even though the oxygen content remained above 10 percent.
2. At a higher temperature in the secondary combustion chamber (810°F, 430°C), the introduction of a larger amount of propane was more effective. The CO level of 0.5 percent did not change appreciably, but the THC was reduced from 4100 to 1600 ppm, and the oxygen content was reduced from 16.0 to 6.4 percent. The propane burning was apparently essentially completed.

TABLE 5. EFFECTS OF SECONDARY COMBUSTION ON EMISSIONS
Burning Fir Brands at Approximately 30 lb/hr

	Prior to Secondary Burning	After Secondary Burning Initiation	During Secondary Burning	After Secondary Air Flow Stopped
Time, hr. min.	15:10	15:13	15:59	16:01
Flue Gas Composition, as Measured				
O ₂ , percent	3.6	4.6	7.6	5.37
CO ₂ , percent	15.1	14.6	13.0	14.3
CO, percent	2.3	0.1	0.1	1.51
THC, ppm	8200	680	430	4100
Temperature in °C	613	712	656	617
2nd Comb Zone, (°F)	(1135)	(1314)	(1212)	(1143)

3. At very high temperatures in the secondary combustion chamber (1400°F, 760°C), the introduction of propane was even more effective. The CO level was reduced from 1.5 to 0.3 percent and the THC was reduced from 2400 to 400 ppm. The quantity of propane required to produce these reductions was small, resulting in only a 90°F (50°C) temperature increase and a slight O₂ reduction to 6 percent.

The stove conditions during these observations were not very stable, with appreciable gas composition and temperature fluctuations. Because of this, the data noted above are each averages of 5 one-minute readings taken just before or just following the initiation of propane introduction. Though crude and preliminary data, these do show that auxiliary fuel can in some situations reduce the emission of CO and organics.

The use of an afterburner with an external air source would reduce emissions if the gas and air flow rates were high (compared to the total wood emissions flow rate). This combustion would be very uneconomical if it is placed near the exit of the stove. Another option would be to have a control system that would regulate the amount of fuel and air. This would be an expensive installation and might have high maintenance costs.

Thermostatic Control

Many stoves on the market today have a thermostatic control. The thermostat consists of a coil of a strip of bimetal linked with the primary air damper. This permits the operator to set the stove at desired and reproducible operating condition for unattended operation. As the stove heats up the coil will deform, lowering the damper and cutting back on the primary air, thus reducing the temperature.

A stove with a thermostat was loaded with a large charge of wood and monitored for two hours. The thermostat was set at the medium setting and allowed to operate without any disturbance.

During the first hour everything was fairly steady. After which time the control system started to cycle. The thermostat closed the primary air damper, lowering the oxygen level and raising CO and THC emissions,

and lowering the outlet temperature of the stove. After 10 minutes the damper opened allowing temperatures to increase and emissions to decrease. The thermostat again started to close the damper as the wood was depleted. Even though the emissions and temperature were starting to oscillate the last hour of the test, the burning rate was steady.

OPERATOR FACTORS

During the operation of a wood burning stove, there are factors that effect emissions over which the operator has direct control. These are the amount of wood placed into the stove, the way the wood is placed in the stove, and the burning rate at which the stove is operated. The effects of mass of charge and burning rate on emissions have been reported by Butcher (19).

Amount of Wood Charged

The amount of wood placed into the stove at one loading will have a large influence on the amount of pyrolysis products leaving the stove. The emissions go up when more wood is within the stove, even at the same burning rate, due to the increased quantity of wood exposed to the heat and thereby subject to preburning pyrolysis.

To demonstrate the effect of increased wood inventory in a stove two tests were run. In one test, 12.9 pounds were burned and the other test burned 41.9 pounds of wood. The same triangular wood pieces were used (oak 4 x 4's) and the stove was operated at the same air setting during the same day. The tests were run using the sidedraft mode of burning discussed earlier in the text.

Table 6 shows the comparison of the two tests, demonstrating that as the wood inventory is increased the emissions increase. The burning rates for the two tests were essentially the same but the large charge resulted in approximately doubling the emissions.

TABLE 6. EFFECTS OF SIZE OF CHARGE ON EMISSIONS
Side Draft Burning of Oak 4 x 4's

Test Run Number	34	35
Mass of Charge, lb	12.9	41.9
Burning Rate, lb/hr	17.4	19.2
Excess Air, percent	62.9	58.1
Stack Temperature, °F (°C)	680 (360)	660 (350)
Gas Composition as Measured,		
CO, percent	1.2	2.5
THC, ppm	2800	5300
Emissions, lb/1000 lb wood		
CO	100	220
THC	15	26

Any approach that keeps the wood from pyrolyzing while it resides in the stove prior to active burning should reduce emissions. The only course open to the operator to reduce emissions from this mechanism is to add small quantities of wood more frequently.

Wood Placement in Stove

How densely and where the wood is placed in the stove can affect emissions and are controlled by the operator at the time of loading. The wood placement in the stove controls the path of the primary air within the stove. If the wood is packed densely, the primary air cannot reach the internal surfaces of the wood in the pile, allowing the pyrolysis of the wood to take place without sufficient air to burn. The location of the wood with respect to the entrance of the primary air can allow the air to bypass the combustion zone and exit the stove resulting in high excess air and high emissions.

There were no quantitative tests conducted to determine the effect of location or loading density on emissions. However, it was observed in tests where the primary air entered through openings in the side of the stove and the wood was placed over a bed of hot coals in a manner that reduced the surface area exposed to the incoming air, the wood burning rate was low and the excess air was high, as indicated by O_2 content in the flue. The wood that was left unburned late in the burning cycle was the wood in the area where the wood had been the most densely packed. In stoves where the wood was placed directly on a hearth with no provision for air to get under the wood, it was found that the wood had to be piled loosely so that air could get through the wood to allow for complete combustion of the pyrolysis products and to achieve the desired burning rates.

Burning Rate

The rate at which the wood is consumed in a stove is known as the burning rate and in this report refers to actual weight of wood as fired, not the dry weight. Higher stack temperatures usually accompany higher burning

rates, and this observable characteristic may be used to correlate burning rates on different stoves. Most stoves are designed to operate over a wide range of burning rates. In this program, as in conventional service, the wood burning rates in the naturally drafted stoves were arbitrarily controlled by restricting the primary air inlet to the stove, i.e., closing the air inlet damper to reduce the rate of burning. At the lower burning rates the oxygen concentration in the flue gas in many stoves is higher than at higher burning rates, indicating a larger amount of excess air for the fuel that actually burned. This seemingly anomalous trend presumably results from a larger fraction of the total air bypassing the active burning at the low burning rates. Thus, at the lower rates the primary burning is even more severely air limited than the stack gas analyses would indicate. This results in the lower temperatures and the increased emissions of combustibles.

It became evident early in the program that the emissions of CO and organics (as indicated by THC) were very dependent on burning rate. Figures 12 and 13 show this effect for three modes of burning in one stove (Defiant). The data plotted for the downdraft mode have not been connected by lines to form a curve, but the similar effect is evident. This effect has been noted by others (19). Very high emissions associated with low burning rates (hold-fire conditions) were observed in this program and a related TVA program when average burning rates were maintained below about 10 pounds per hour. Presumably, the same effect would be observed in smaller stoves when operated at correspondingly lower rates of burning.

FUEL PROPERTIES

An operator has some control over the fuel properties of the wood that is used. The wood can be bought seasoned or the operator can season it. Where and how the wood is stored is also under the influence of the operator. The size of the wood can be decreased by splitting or sawing. The type of wood is controlled by its availability in the area. The effects of the fuel properties are discussed in the following paragraphs.

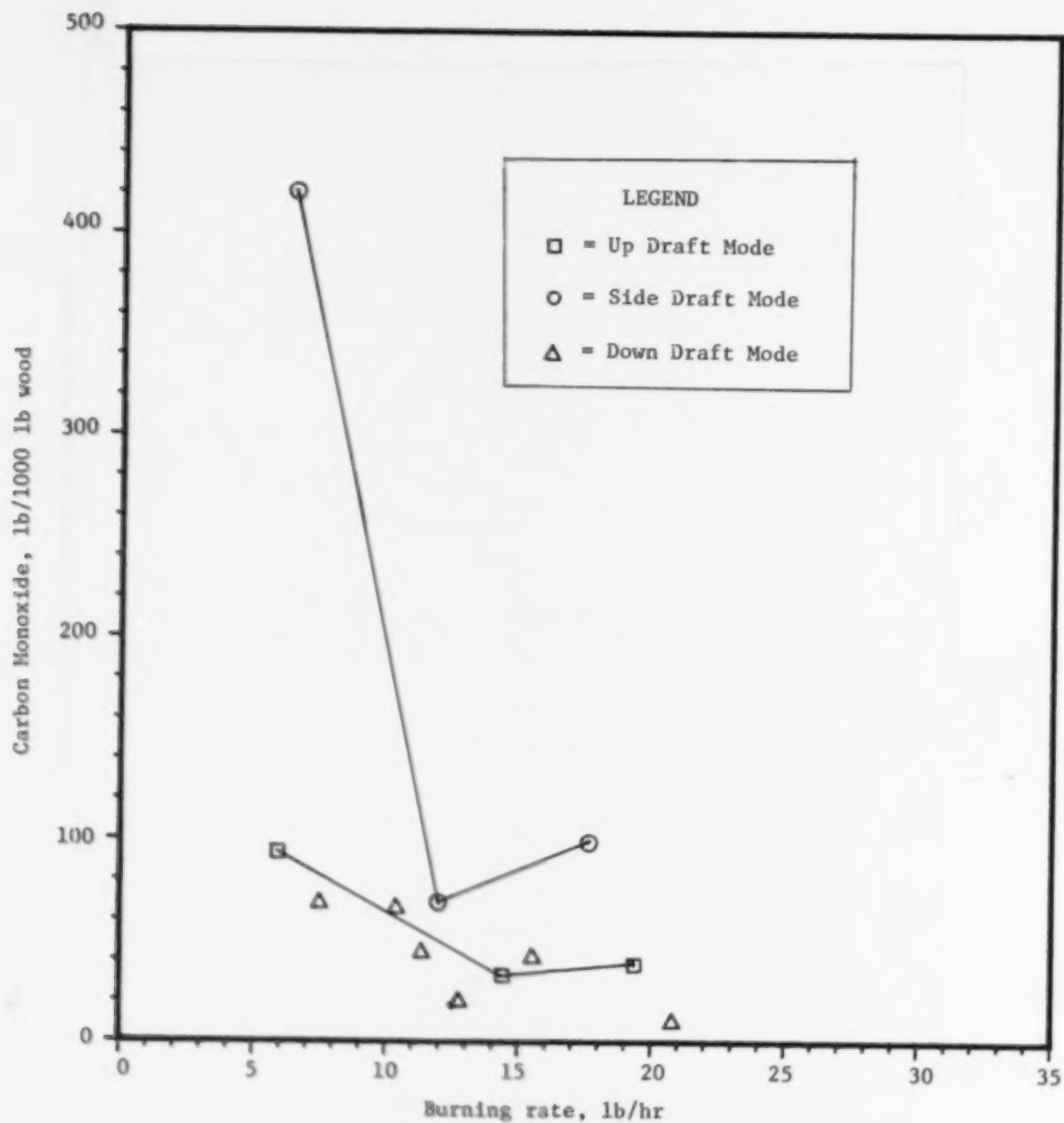


FIGURE 12. CO EMISSIONS FOR ONE STOVE, THREE MODES OF BURNING.

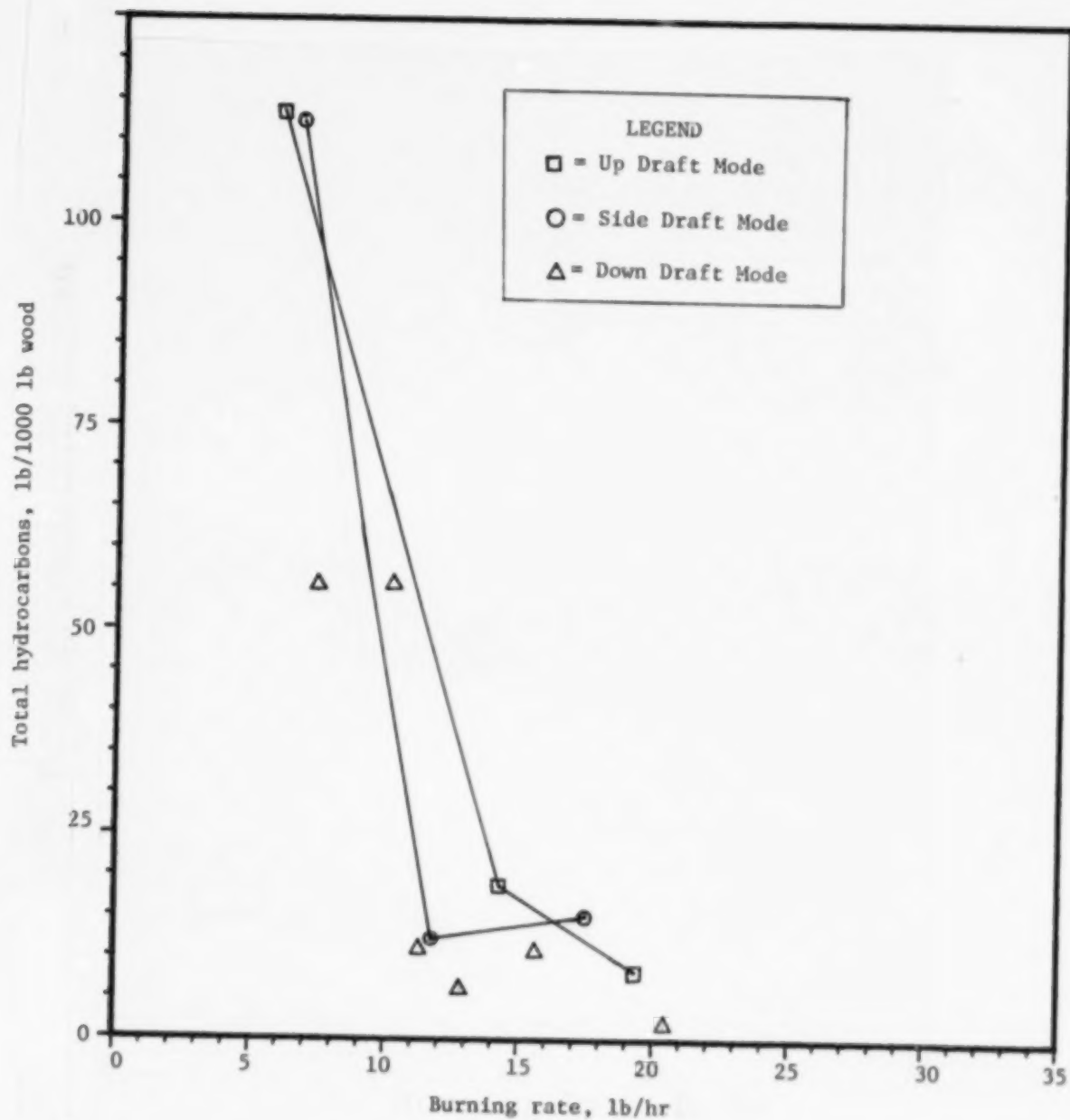


FIGURE 13. THC EMISSIONS FOR ONE STOVE, THREE MODES OF BURNING.

Moisture Content

The moisture in wood is dependent upon the type of wood and the amount of time it has been dried (seasoned). The water in the wood increases the amount of heat required to raise the wood to its combustion point. This reduces the rate of pyrolysis until the moisture is released from the wood.

For investigating the effects of moisture, oven dried Douglas Fir brands were soaked in water for different periods of time to provide different moisture contents. The three different moisture contents were 0, 14, and 28 percent on a wet basis. All tests were run in the downdraft mode of burning with a bed of hot fine coals on the grate, two to three inches thick, at the start of the test. There was also a test run using oak soaked in water to increase moisture content from 21 to 31 percent, and split pine logs oven dried to remove all free moisture (see Table 2).

Table 7 shows the effects of the augmented moisture content on the emissions, with no distinct trends evident from these limited tests.

Wood Size and Shape

The size of wood has a large effect on the rate of pyrolysis. The smaller pieces of wood result in: a shorter distance for the pyrolysis products to diffuse, a larger surface area to mass ratio, and a reduction in the time required to heat the entire piece of wood. The heat transfer coefficient is generally twice as high for with-the-grain transfer as opposed to across the grain transfer. Therefore split wood will become heated and pyrolyze quicker than unsplit wood of the same size under the same conditions.

The effects of size and configuration were investigated in tests burning cured oak in the downdraft mode. The stove was run at the same conditions for each test, so the burning rates were different, dependent only on the wood. The smallest wood used was oak kindling which was four to six inches long and had an equivalent diameter of about one inch. It was all split, there were no round sticks used. The other three configurations had the same length (11 to 14 inches) with an equivalent diameter as indicated in Table 8. The differences were; the split wood was triangular and was split from large round pieces of oak without bark, the

TABLE 7. EFFECTS OF WOOD MOISTURE CONTENT

Burning Mode Fuel Used	Down Draft Oak Logs		Down Draft Fir Brands		Up Draft Pine	
Moisture Content, % wet basis	21	31	0	14	28	0 42
Burning Rate, lb/hr	11.3	9.8	14.0	10.7	18.0	20.7 21.6
Gas Composition as measured						
CO, percent	0.3	0.1	0.3*	0.4	0.4	3.9 2.0
THC, ppm	900	1500	1100*	900	2000	9100 7100
Emissions, lb/1000 lb wood						
CO	48	39	67	74	49	330 120
THC	11	34	16	9	16	44 25

* Secondary air rate was changed several times during this test, but no evidence of secondary burning was observed on the continuous recording monitors.

TABLE 8. EFFECTS OF WOOD SIZE
AND SHAPE ON EMISSIONS
Fuel: Air Dried Oak

Test Run Number	61	62	60	63
Wood Size, equivalent diameter, inches	2.1	2.1-3/4	2.8 (4 x 4 triangular)	4
Shape	split	split	sawed	rounds
Burning rate, lb/hr	19.1	11.3	18.4	12.8
Gas Composition as measured				
CO, percent	1.0	0.3	0.5	0.1
THC, ppm	1600	900	1000	600
Emissions lb/1000 lb wood				
CO	110	48	61	19
THC	10	11	7	7

4 x 4 wood was triangular and was sawed from 4 x 4's cut diagonally, the rounds were round oak logs, the bark was left on. All tests burned about the same amount of wood (14 to 16 pounds).

Table 8 shows the emission data. As expected, the split kindling resulted in the highest emissions, the larger round pieces had lowest emissions. These data are shown in Figure 14, together with the same emission data from test 58 burning dry fir brands.

Wood Type

The differences in ultimate analyses of wood on a dry basis (carbon, hydrogen and oxygen) are within one to two percent for the majority of all wood species. The more important differences between woods arise from moisture, density, and heating value. The inherent difference between soft wood and hard wood is the amount of resins that are contained in soft woods, which increases their heating value on a weight basis.

In two popular stove configurations, updraft and sidedraft, burning of green pine resulted in slightly lower emissions than the dried oak 4 x 4 fuel. The one test conducted with the same pine fuel after being oven dried, to nil moisture content resulted in emissions only slightly higher than the oak 4 x 4 fuel. The relatively lower emissions for the green pine presumably result from the delayed pyrolysis associated with the moisture content, whereas the dried pine pyrolyzed at a higher rate resulting in the increased emissions. Table 9 summarizes these comparisons.

Charcoal was burned in the down draft mode to demonstrate the effects of a wood based fuel with very low volatile matter (Test Run 76). As expected, the emissions for both total hydrocarbons and carbon monoxide were the lowest of all test runs as shown in Table 1.

POLYCYCLIC AROMATIC HYDROCARBON EMISSIONS

The emissions of PAHs from the three burning modes in the naturally drafted radiant stoves are shown in Table 10. The differences between the three burning modes while burning oak was not great. The emissions for down-

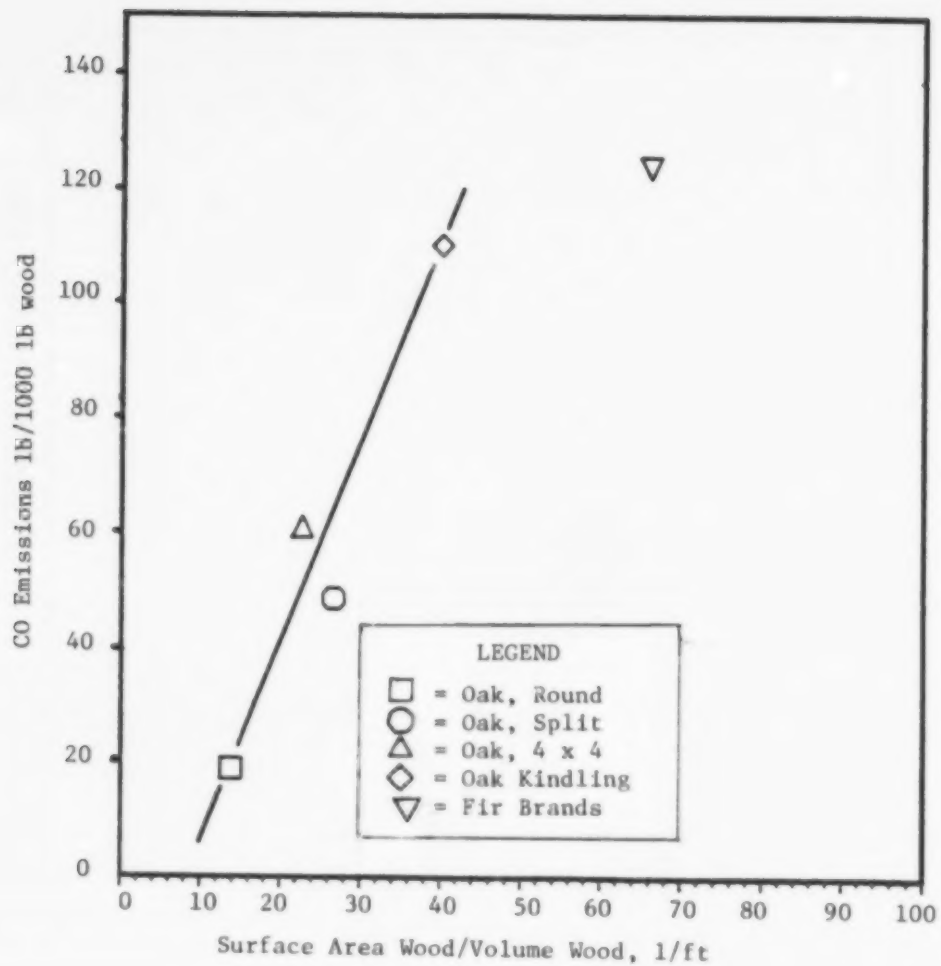


FIGURE 14. EFFECT OF WOOD SIZE ON CO EMISSION FACTORS.

TABLE 9. EMISSIONS FROM BURNING
GREEN PINE

Burning mode	Updraft, with grate			Side Draft	
Fuel Used	Oak 4 x 4	Green Pine	Dried Pine	Oak 4 x 4	Green Pine
Burning rate, lb/hr	20.9	21.6	20.7	18.7	18.4
Gas Composition, as Measured					
CO, percent	2.7	2.0	3.9	2.5	0.5
THC, ppm	5900	7100	9100	6200	1800
Emissions, lb/1000 lb wood					
CO	270	120	330	190	40
THC	34	25	44	28	9

draft burning ($50 \text{ lb}/10^6 \text{ lb wood}$) was about 3 times the emissions of updraft burning with a grate ($18 \text{ lb}/10^6 \text{ lb wood}$). The side draft burning was intermediate, in PAH emissions, with wet pine producing a slightly higher factor than dry oak. This difference is reversed for the emissions for Benzo(a)pyrene (BaP), a very toxic constituent of the total PAH mixture. The BaP emissions measured for updraft burning ($1.4 \text{ lb}/10^6 \text{ lb wood}$) were higher than that from sidedraft burning, and much higher than from down-draft burning ($0.38 \text{ lb}/10^6 \text{ lb wood}$). The sidedraft mode was intermediate again, with wet oak and dry pine producing 1.2 and $0.52 \text{ lb}/10^6 \text{ lb wood}$ burned, respectively.

When burning split oak logs in the high turbulence burner, appreciably lower emissions were observed than with either of the more conventional stove designs. Details of the measurements, techniques, and experimental observations of PAH emissions are presented in more detail in Appendix C.

COMMERCIAL HIGH TURBULENCE BURNER

The commercial stick burner was made to burn very efficiently by utilizing a high turbulence level and other techniques as noted earlier (see page 23). It was operated as prescribed by the manufacturer burning stick wood. When the burner was fired with 4 very large split logs, one jammed in the hopper and remained partially unburned. When fired with the recommended size of split logs, operation was reliable with low emissions. When fired with smaller sizes of split logs the emissions increased only slightly. Table 10 shows the measured emissions when the burner was run until the blower was automatically turned off. When operating properly the emissions are appreciably less than from the two typical radiant stoves. Even when burning brands to deliberately maximize early hydrocarbon emissions or when faulty fuel performance was encountered, the THC emissions were not as high as from the more conventional radiant stoves. The low CO emissions, when properly burning the more appropriate split oak logs, is also much lower than from the radiant heaters.

These data demonstrate how appreciable reductions in emissions can be obtained with the application of several combustion modification techniques. Unfortunately, many of these techniques are not applicable to the naturally drafted radiant stoves, without extensive system redesign.

TABLE 10. EMISSIONS FROM HIGH TURBULENCE BURNER

Fuel Burned	High Turbulence Burner				Comparable Updraft Stove With		Comparable Side Draft Stove	
	Large Split Oak Logs	Split Oak Logs **	Small Split Oak Logs (4" edges)	Dry Fir Brands	Grate Dry Oak 4 x 4	Grate Dry Oak 4 x 4	Dry Oak 4 x 4	Dry Oak 4 x 4
Burning Rate, lb/hr	22.1*	24.1	21.9	20.9	16.5		18.7	
Excess Air, %	220	920	110	120	40		42	
Gas Composition as Measured,								
CO, %	0.6	0.1	0.3	1.6	3.6		2.5	
THC, ppm	2000	200	300	1900	7100		6200	
Emissions, lb/1000 lb wood,								
CO	97	25	30	222	280		190	
THC	18	5	2	16	32		28	
PAH	ND	0.011	ND	ND	0.018		0.035	
Stack Inlet Temperatures,								
°F	247	343	331	285	950		703	
(°C)	(119)	(173)	(166)	(141)	(510)		(393)	

* = This run terminated with 31% of fuel unburned. One log jammed in the hopper and did not fall into the burning region.

** = Sizes of split logs recommended by manufacturer.

ND = Not determined.

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APPENDIX A

EMISSION MEASUREMENT PROGRAMS

In the course of this project a search has been conducted to identify programs in this country in which actual measurements of stove emissions have been or are being made, wherein some correlation is possible with stove design and operating conditions. The programs are few, and there has been no consistency in the experimental techniques used for

- Stove installation
- Stove operation
- Sampling of emissions
- Analysis of collected samples
- Interpretation of the results

The programs have used different fuels burned in different stoves with different firing techniques, all of which have generally been adequately described.

Major problems exists in the characterization of the chimney and draft systems used which have significant effects on both stove operation and ultimate emissions, and emission sampling systems used which arbitrarily separate gaseous from particulate emissions depending on the temperatures of the point of particulate capture and retention. Although the measurements and observations of emissions have been related to stove parameters, these other factors can materially affect the emissions as measured.

Monsanto Research Corp.

This organization has conducted the most extensive analysis of emissions from residential wood burning equipment. The tests were conducted early in 1979 at Auburn University. The University staff operated the stoves and measured the efficiencies, and Monsanto staff conducted the measurement and analysis program. Two similar stoves and a fireplace were operated burning both pine and oak cardwood, using both seasoned and green wood. In addition to the normal combustion gasses (O_2 , CO_2 , SO_x , NO_x , and CO), the emission measurements included particulate matter, condensable organics, volatile organics, aldehydes, major organic species, and polycyclic organic species. The tests were all operated at relatively high burning rates, and did not demonstrate the effects of burning rate on emissions.

The effects of wood type and moisture content were shown to be generally low, with green pine producing particulate and organic emissions slightly higher than the other three woods burned. Many POM species were identified in the stack emissions (particulates and gases samples combined) and bioassays of these specimens were found to be both mutagenic and cytotoxic.

This program was managed by D. G. DeAngelis of Monsanto under EPA IERL/RTP sponsorship.

California Air Resources Board

This agency has conducted tests in 1977 on two free-standing stoves in both residential and laboratory test installations. Fuels used were oak, pine, and coal, and relatively high burning rates were maintained with frequent additions of wood. Particulate emissions were determined using EPA method 5. Bag samples were used for total hydrocarbon and other gaseous determinations at another location using gas chromatography.

These tests were conducted by Peter Kosel of the Stationary Source Control Division of the Air Resources Board.

Bowdoin College, Maine

This experimental program has focused on particulate emissions at low burning rates. All emitted particulate matter was collected on a filter after the flue gas has been cooled and diluted with large quantities of fresh air. No gas composition or excess air measurements have been made. The implications of the particulate collection system is that all organic emissions condensable at ambient conditions will be collected as particles. Approximately half of the particulate matter collected has been benzene extractable. Nearly half of this extractable material is neutral with regards to acid-base extraction procedures, and this fraction would presumably contain the polycyclic emissions.

This study has shown that the particulate emission factor varies proportionally with the weight of the initial fuel charge and with the reciprocal of actual burning rate.

This program has been led by Professor S. S. Butcher, and the results published in the APCA journal. Support has been received from the State of Maine.

Canadian Combustion Research Laboratory

This laboratory has conducted emissions analyses and efficiency tests on wood stoves of different generic designs. Continuous measurements are made of CO, CO₂, O₂, NO_x, and total hydrocarbons. Split cordwood has been burned at relatively low rates (< 50,000 Btu/hr) while overall thermal efficiencies have been determined by the stack gas (indirect) method.

The results to date indicate that overall efficiencies fall off at the higher burning rates, even though the emissions of CO and THC per pound of wood burned decreases and the combustion efficiency increases. Their comparison of generically different stoves shows a general increase in emissions of CO and THC (lb/lb fuel burned) as the burning rate is reduced. Large variations in emissions between different designs of up draft stoves were observed.

This study is led by ACS Hayden and R. W. Braaten for the Department of Energy, Mines and Resources, Ottawa, Canada.

Del Green Associates, Woodburn, OR

This company has just started a program for Region X U.S. EPA concerned with wood stove utilization in their area. The multi-task program includes a source sampling task to (1) determine effects of wood moisture content on emissions, (2) develop simplified testing procedure, and (3) develop reasonable standards for stove emissions using 6 stoves in their program. Another task includes indoor air pollution measurements in a few residences heated by wood burning within the living space.

This program is being led by Norman Edmisten with cooperation from OMNI Environmental.

Auburn University - Auburn Alabama

The Mechanical Engineering Department of Auburn has conducted research on residential wood burning equipment for several years. This work has focussed on the measurement and characterization of stove performance, and the safety of wood stove operation including creosote problems. They have developed extensive facilities and capabilities for measuring stove efficiency and heat output rate. Their emission measurements are normally limited to O₂, CO₂ and CO as manually determined from grab samples by Orsat.

Auburn's program for improving the efficiency, safety, and utility of woodburning units has been sponsored by DOE and has been led by Professors Glennon Maples, David Dyes and Timothy Maxwell. They have also been active in developing wood stove evaluation techniques in conjunction with the ASHRAE and the Fireplace Institute, and conduct the Fireplace Institute's experimental evaluation program.

Argonne National Laboratory, DOE

This laboratory has an ultimate objective to develop emission factors for residential wood stoves. Their experimental program includes an investigation of stove design characteristics that affect emissions, and the development of techniques and instrumentation to measure and characterize these emissions.

Their experimental program involves three stoves in a laboratory facility with on-line CO and CO₂ measurements. Stack samples are obtained with cold traps, and analysis of POMS is with GC/MS.

Their preliminary measurements have focused on low burning rates (air inlets 10 to 25% open). With above-bed temperatures below 400°F, no polycyclic species have been detected. More recently traces of naphthalenes have been observed.

John Harkness is leading this program at Argonne as an in-house study for DOE. No publications describing emissions have been issued to date.

Tennessee Valley Authority

This agency initiated an experimental evaluation of several wood stoves proposed for customer use in regions of their utility district. The program was initiated with the measurement of efficiency by the indirect method, and emissions using on-line instrumentation. The stoves were fired with kiln-dried fir brands, using the UL batch burning procedure in which a test consists of burning a fresh charge of brands to 95% completion on a weight basis. Three rates of burning were maintained for each stove in separate runs.

After a destructive fire occurred at the TVA facility in Chattanooga, Battelle conducted additional tests for TVA at Battelle's Columbus Laboratories. These continued tests were modified to include the burning of air-dried oak in larger triangular pieces, simulating typical residential split cordwood. The results of some of these tests have been used in support of this EPA program at Battelle.

The TVA program has been actively managed for the Solar Applications Branch of TVA by Dr. Jerry Harper. No publication of these studies has been made to date.

Virginia Polytechnic Institute

This university has an active program related to control of emissions from wood stoves. Their three phases include:

(1) Data acquisition facility development

Their facility includes on line continuous measurement of O₂, CO₂, CO, NO_x, and stack gas flow measurement.

They plan to incorporate a hot FID instrument for total hydrocarbons.

(2) Catalyst bed afterburner

This development is focussed on a bed type unit for stack installation rather than within the stove.

(3) Staged combustion studies

This effort is to determine experimentally what conditions are necessary and sufficient to assure secondary combustion without auxiliary fuel. This phase is focusing on gas composition, temperatures, and mixing rates.

This program has not resulted in any published results, although catalysis tests have been run.

Dr. Dennis Jaasma is conducting this program primarily supported by University funding although a limited industrial grant has been received. They are seeking support for continuation of the program.

National Bureau of Standards

The center for Fire Research, NBS, in conducting a study of "Gaseous and Liquid Combustions Products from Wood Burning Devices". The objective is to provide data and techniques to support combustion modification efforts. The emphasis is to be placed on detailed physical and chemical characterization of the emission products as affected by time during a burn cycle, type of wood, moisture content, and excess air. Both within firebox phenomena and within chimney effects are of concern.

This study is to be led by Dr. Richard Gann, NBS, on funding provided by DOE. No published data has been generated by this program.

Thermocore, Inc. Lancaster, Pa.

This company has attempted to improve stove thermal efficiency (including combustion efficiency) by means of altered air supply, focussing on preheating of the air, and alternative paths for air entry into the stove. Their experimental program included extensive temperature measurements with thermocouple recordings maintained throughout batch type test runs. Their emission measurements were limited to Orsat analyses made at several times during the burning of a large charge of wood. No combustibles were measured by Orsat, and hydrocarbon emissions were estimated by visual plume observations.

Yale Eastman managed this program under the sponsorship of the Philadelphia office of the DOE. Their report has been submitted to DOE, but not released in any form for publication.

New York University of Plattsburgh

This program of stove development has focussed on overall efficiency and particulate emissions as affected by stove design, operating procedures, and controls development (thermostatic). The emission measurements have been limited to particulates as measured by collection on a cooled but not temperature-controlled filter from stack gasses withdrawn through a probe. The velocities of specimen withdrawal and stack flow are measured by hot wire anemometers, with sampling velocities greatly exceeding stack velocities. Particulate collections have been made using one minute sampling periods at 10 minute intervals through out run periods of several hours. Stove operation has generally been at very low burning rates, i.e., stove exit temperatures 140 to 500°F.

This program has been conducted by Professor Stockton Barnett with personal and internal funding, and outside support is being sought. No results have been formally published.

Vermont Environmental Control Agency

This agency has been conducting a field measurement program of the ambient environment in an area where residential heating is extensively supplied by wood stoves. The community has no large industrial sources, and an extensive inventory has been conducted to determine the true extent of wood burning for residential heating. The principal emphasis is on the determination of the contribution of wood burning to the total particulate loading, as determined by analysis of the particulates caught on hi-volume samplers placed around the community. Microscopic observations of the particulates are being made to determine their source or origin. Some emission measurements have been made at residences using a Rader High Volume Sampler and an EPA Method 5 sampler. The organic materials penetrating the Method 5 filter have been measured by extraction from the back half impingers, but these materials have not been analyzed to determine their specie composition.

Cedric Sanborn is conducting this program with state agency support.

Institute of Man and Resources

This organization has conducted a field demonstration program of ten different residential furnaces. The emission measurements included CO, NO_x, SO₂, and particulates, with short time emissions measured under all operating modes of each unit. The particulate measuring system consisted of diluting and filtering the entire flue gas stream in the manner used by Butcher. The particulate samplers operated at temperatures below 100 C, and sampled for periods up to 10 minutes. The filter catch was extracted with benzene and dried to determine the condensable organic content which varied from 13 to 51 percent of the total particulate matters collected.

The emission test program was conducted for the institute by Atlantic Analytical Services Ltd., Saint John, N.B. and led by Alex Graham. The overall program received support from both provincial and federal Canadian funds, and is coordinated by Rob Brandon.

APPENDIX B

EXAMPLES OF RECORDED TEST DATA

Attached are several typical plots of gas composition measurements throughout test runs. The high concentrations of organics, as indicated by the total hydrocarbon (THC) measurements, are usually accompanied by high CO concentrations as in the up draft and side draft burning modes (Figures B-1 and B-2). These result primarily from the rapid early pyrolysis of the wood after being placed in the stove. The high rate of pyrolysis gas generation, exceeding the local availability of oxygen for complete burning, lasted about one quarter hour in the side draft mode of burning, and for nearly an hour in the up draft mode with airflow through the grate. The latter stages of burning in these two tests consisted primarily of burning the residual char with sufficient local air supply, thus resulting in lower emissions of organics as indicated by THC measurements.

These effects were not observed in the down draft mode, Figure B-3, as the new charge of wood was not as rapidly heated by combustion products in the test shown here, even though a similar charge of wood was placed in the pre-heated stove. The high turbulence burner, Figure B-4, also demonstrated this lack of early pyrolysis, because the wood moved progressively from the cooled upper chamber down into the active primary burning area as burning progressed. The small peak in organic emissions at approximately 0.5 hours into the high turbulence mode test was presumably due to an erratic motion of wood into or within the primary burning area. In these two types of burning, the composition of the fuel actually burning did not change appreciably during the test.

Figure B-5 shows the weight loss record during the side draft burning. It is evident that the weight loss rate was higher during the early stages of burning and generally reduced throughout the test. The rate of heat released, however, did not fall off proportionally, as the early weight loss was associated with relatively low heating value pyrolysis products, whereas the later burning rates were associated with fuel which was primarily char with a higher heating value.

6/10/80 RITEWAY OAK LOGS RUN 77

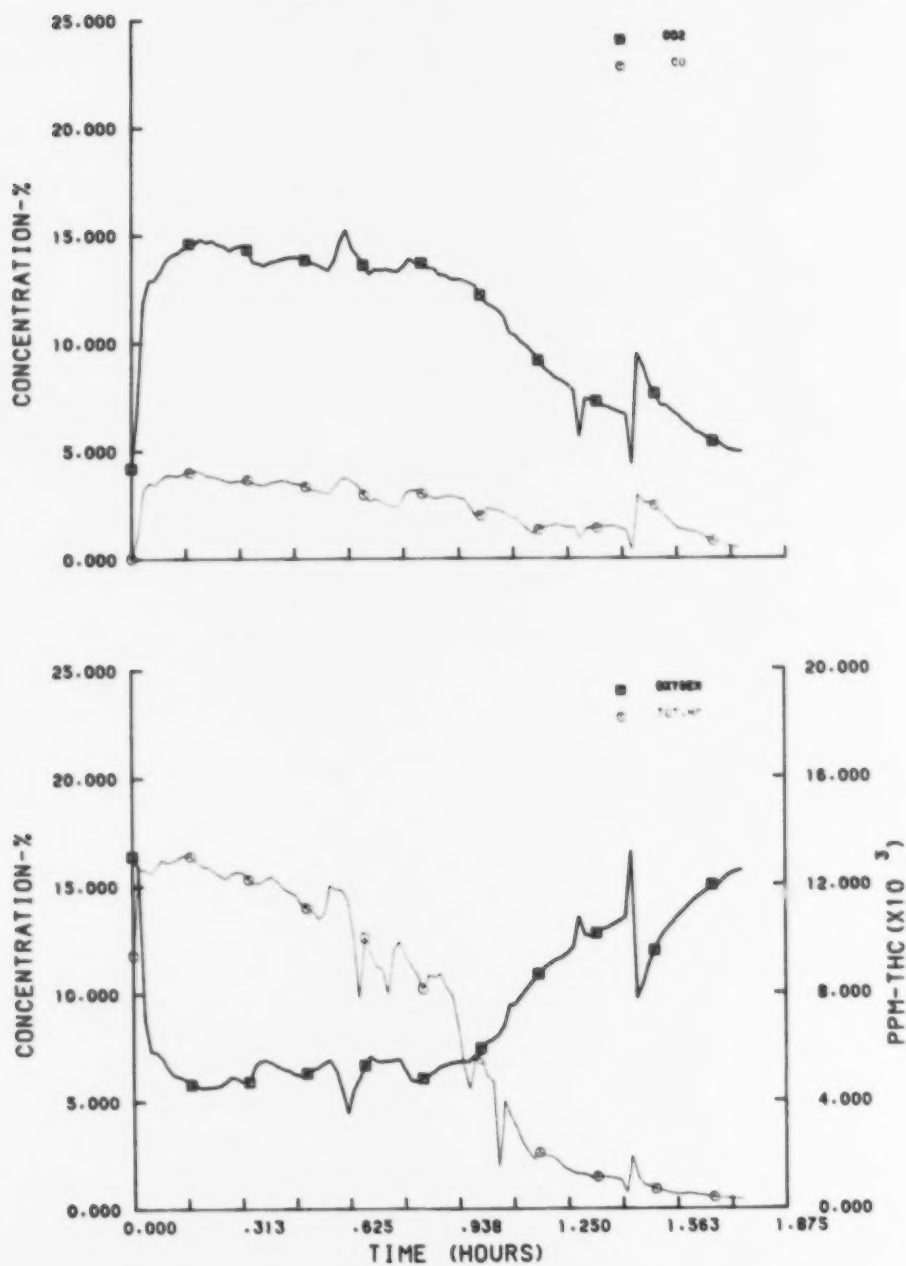


FIGURE B-1. COMPOSITION OF GAS FROM UP
DRAFT BURNING WITH A GRATE
Burning split oak logs
Burning rate 14.4 lb/hr (6.5 Kg/hr).

6/17/80 DEFIANT (SIDE DRAFT) OAK RUN 87

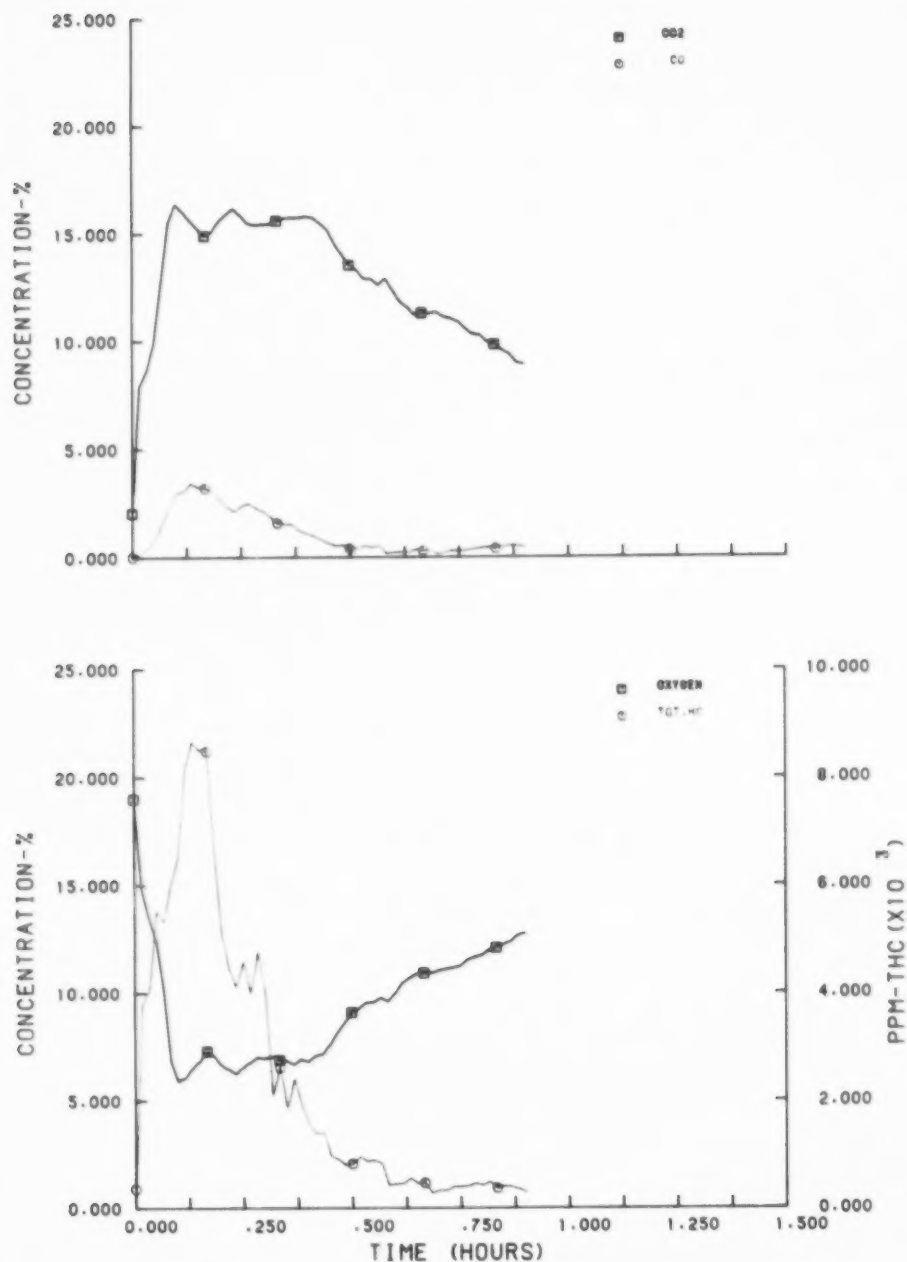


FIGURE B-2. COMPOSITION OF GAS FROM SIDE
DRAFT BURNING
Burning split oak logs
Burning rate 16.6 lb/hr (7.5 Kg/hr).

5/15/80 DEFIANT (DOWN DRAFT) ROUND OAK LOGS N.D.63

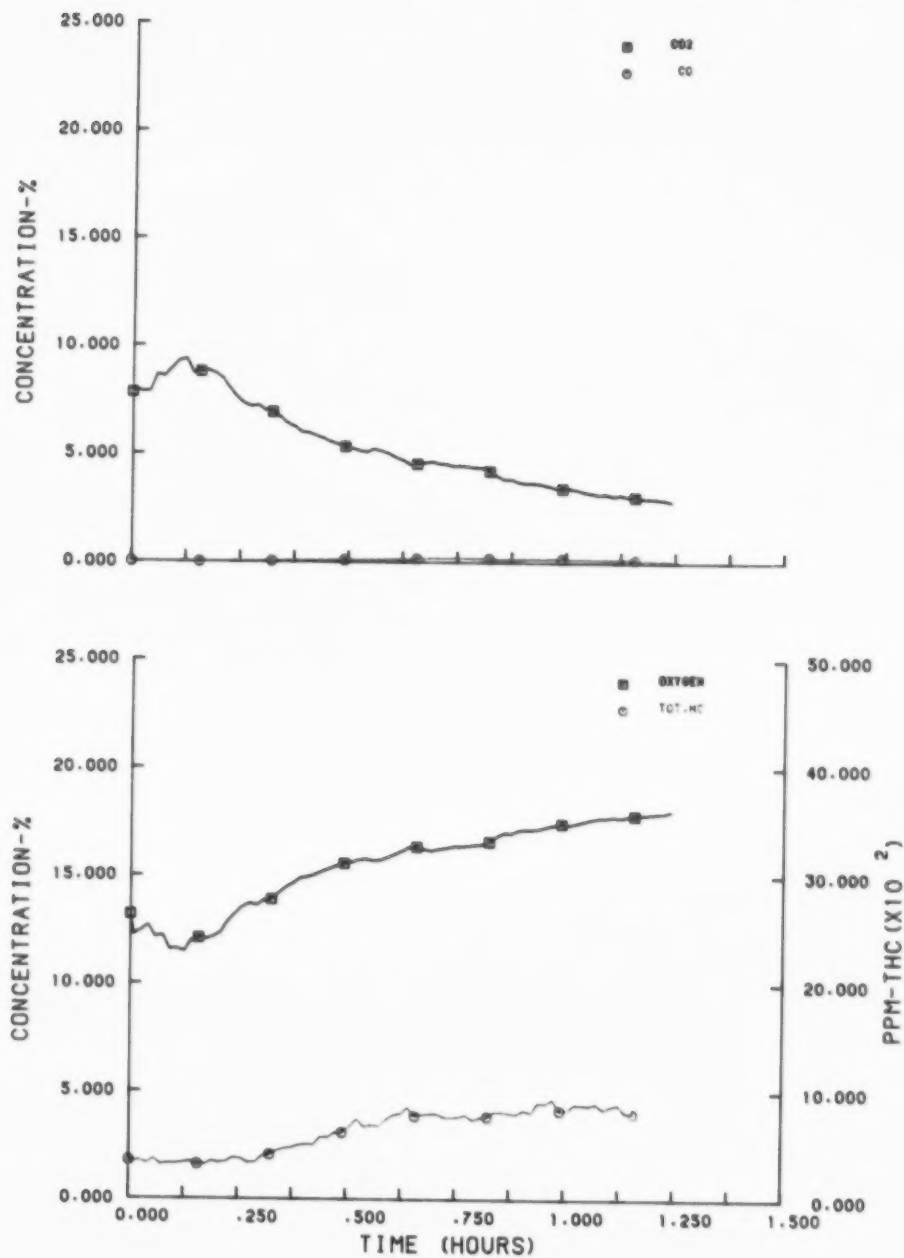


FIGURE B-3. COMPOSITION OF GAS FROM DOWN
DRAFT BURNING
Burning small split oak cordwood
Burning rate 19.1 lb/hr (8.7 Kg/hr).

6/18/80 DUMONT OAK LOGS RUN 91

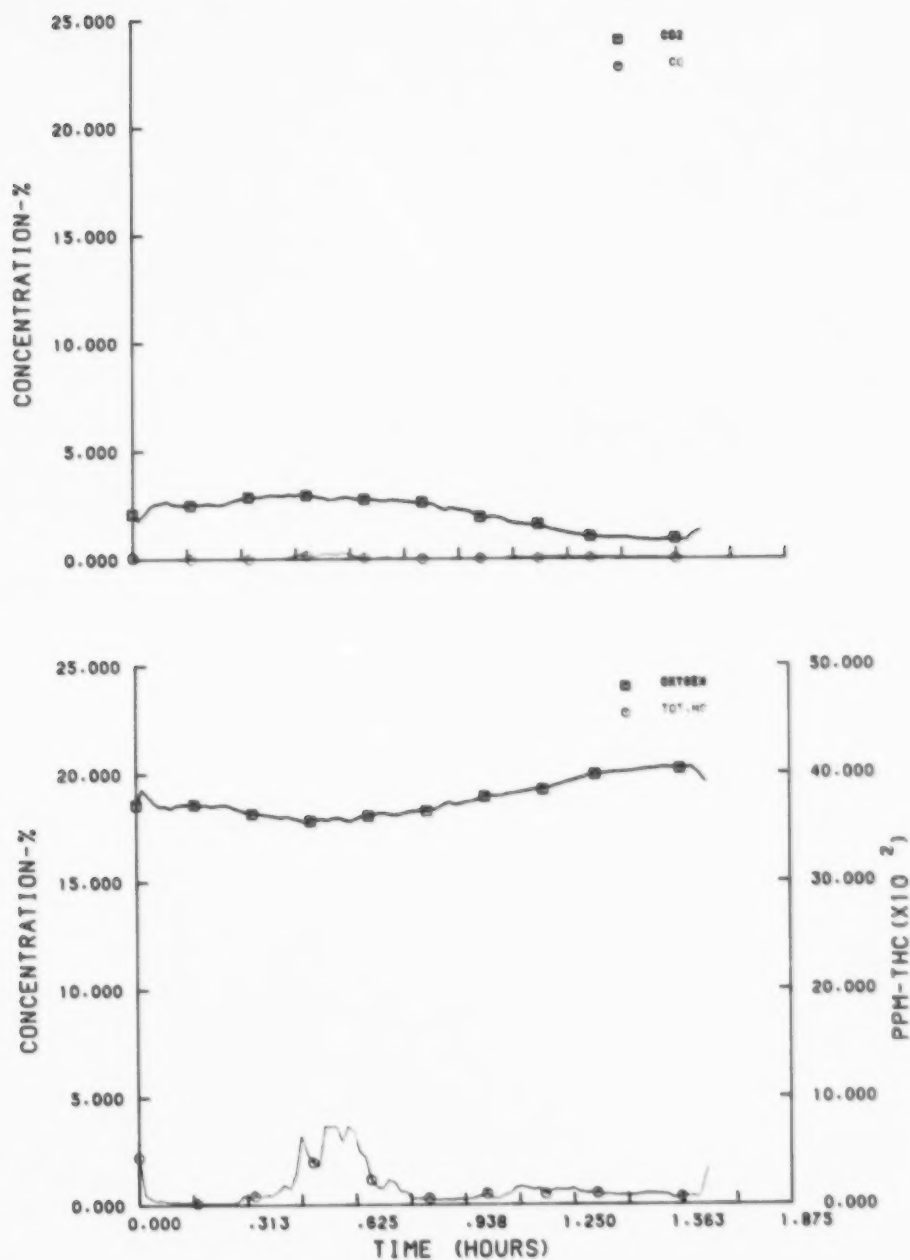


FIGURE B-4. COMPOSITION OF GAS FROM HIGH
TURBULENCE BURNING
Burning split oak logs
Burning rate 24.1 lb/hr (11 Kg/hr).

6/17/80 DEFIANT (SIDE DRAFT) OAK RUN 87

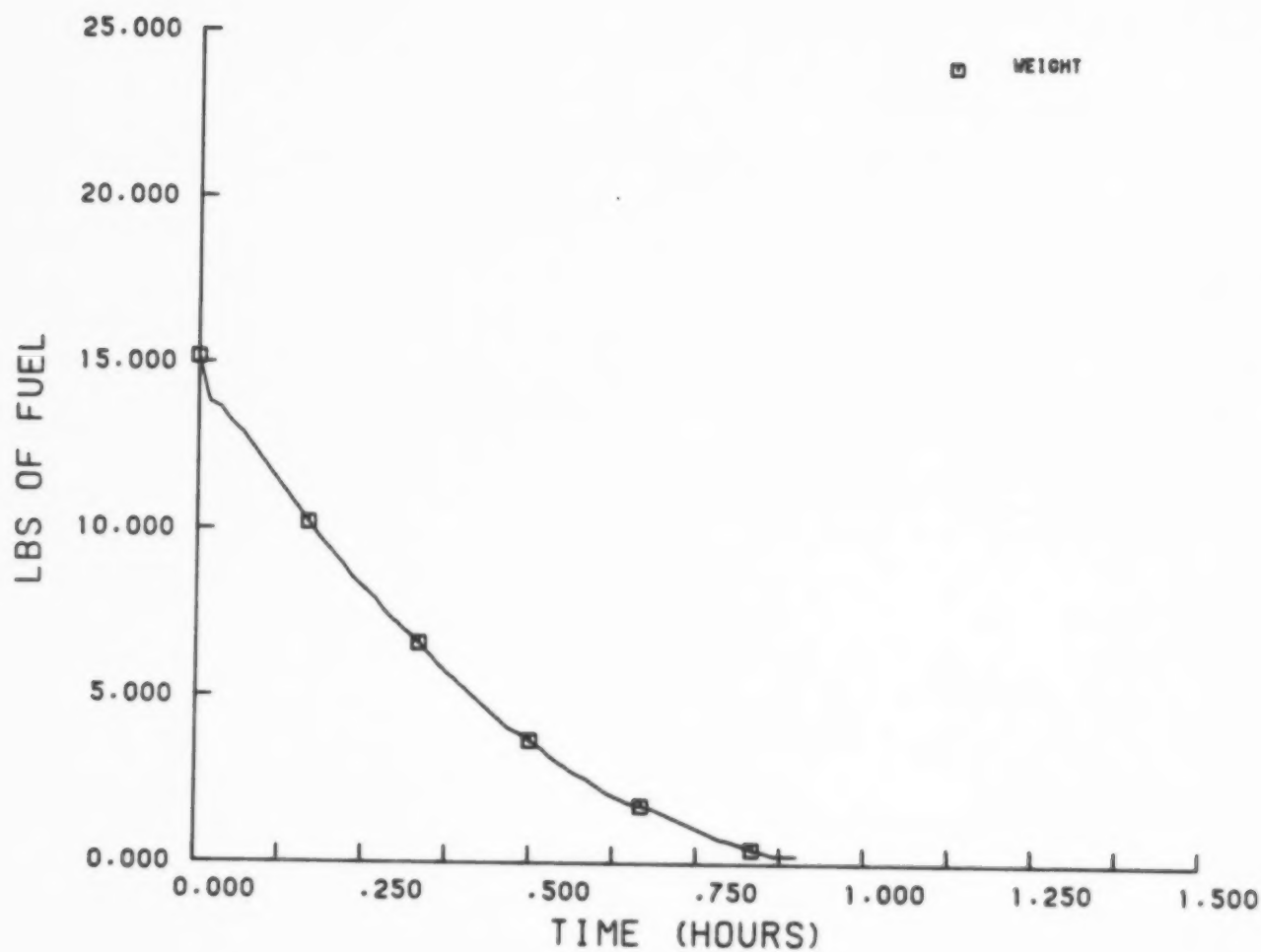


FIGURE B-5. WEIGHT LOSS DURING SIDE DRAFT BURNING
Burning split oak logs
Burning rate: 16.6 lb/hr (7.5 Kg/hr).

BEGIN
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TEXT
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TYPING GUIDE SHEET

CENTER
OF PAGE

TOP OF
IMAGE
AREA

DROPPED
HEAD;
BEGIN
SECTIONS
HERE

APPENDIX C

POLYCYCLIC AROMATIC HYDROCARBON
MEASUREMENTS IN FLUE GAS

Particulate emissions and polycyclic aromatic hydrocarbons (PAH) samples were collected using a Modified Method 5 sampling apparatus. Both the location and configuration of the sampling system were described previously in the experimental section (Section 6). This apparatus allowed the collection of particulate emissions using filtration followed by collection of gas phase PAH by adsorption on XAD-2 resin. Operation of the sorbent sampler and the extraction procedure have been described elsewhere.* The analysis of PAH compounds is complicated by the structural similarity of many members of this class of compounds. Several compounds exhibit positional isomers, e.g., benzo(a)pyrene and benzo(e)pyrene, which coelute on most chromatographic systems. Such isomeric groups often show drastic differences among their members in physiological behavior. For instance, benzo(a)pyrene is known to be a potent animal carcinogen while benzo(e)pyrene is only weakly active. In order to resolve these isomeric groups, high resolution, gas capillary column chromatography coupled to quadrupole mass spectrometry was chosen to separate PAH compounds from these complex mixtures. Single ion monitoring was used to quantify PAHs. Single ion monitoring improved the sensitivity of mass spectral measurements along with providing electronic isolation of fragment or parent ions characteristic of the compound of interest. An additional parameter was used to verify compound identity, the gas chromatographic retention time. From the elution of a set of PAH standards

* Neher, M. B., Jones, P. W., and Perry, P. J. Performance Evaluation of a Solid Sorbent Hydrocarbon Sampler, Research Report EPRI EP-959, Electric Power Research Institute, January, 1979.

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of known purity, a retention time window was determined and quantification was performed only on those compounds eluting at the proper time. Chromatographic and mass spectrometer stability were verified by analysis of the reference standards at the beginning and end of each run of samples. In addition, standards were run in triplicate at five concentration levels to establish the linearity and precision of the analytical curve. The capillary column used for this analysis exhibited a very high chromatographic efficiency as shown by the chromatogram for a test mixture of 21 PAH standards in Figure C-1. The extracts from both filter and resin catches proved to contain a complex mixture of organic species as shown in the GC/FID trace of the particulate associated PAH from a radiant wood stove burning seasoned oak brands and operating in the up draft mode (see Figure C-2).

The specific compounds quantified are listed in Table C-1. It should be noted that several isomeric groups were measured together, e.g., methylanthracenes. Since PAH species often exhibit a simple mass spectral fragmentation pattern consisting of the parent ion, this single ion can be searched at retention times corresponding to known members of the compound class and area responses grouped together for quantification.

The measured levels of individual PAH offer a very interesting comparison of the effect of burn mode on distribution of PAH formed during combustion (see Table C-2). PAH production during combustion of wood is an especially interesting phenomena since neither lignin nor cellulose contain PAH compounds in the raw fuel. The data of Table C-2 show total PAH in milligrams emitted during combustion of a weighed charge of wood. A portion of the flue gas was sampled at the flue gas outlet and the measured PAH concentration was multiplied by a factor representing the total flue gas effluent. Thus, Table C-2 gives the total PAH emissions discharged by the test stoves.

Examining the data in Table C-2, several effects are noticed. The lower molecular weight PAH are found predominantly in the gas phase while the larger molecules tend to be associated with particulate matter. During sampling, the nozzle and filter holder were thermostatically controlled to remain at or above 250°F (121°C), but the flue gas entering the sampler was regularly higher than this temperature. Thus the absolute distribution of PAH between gas and particulate samples is a function of sampling conditions.

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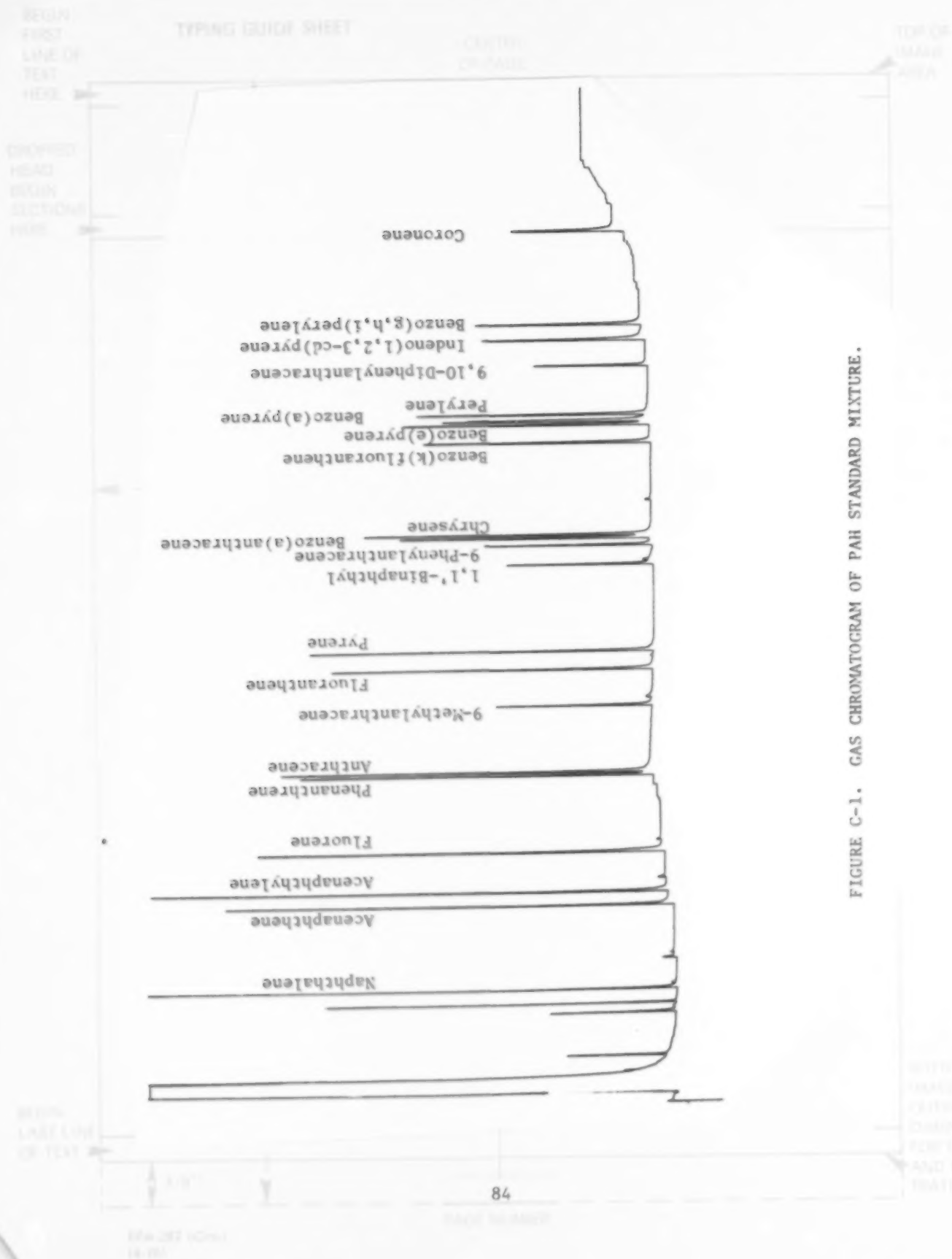


FIGURE C-1. GAS CHROMATOGRAM OF PAH STANDARD MIXTURE.

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FIGURE C-2. GAS CHROMATOGRAM OF PARTICULATE ASSOCIATED ORGANIC COMPOUNDS FROM SEASONED OAK COMBUSTION.

TABLE C-1. POLYNUCLEAR AROMATIC SPECIES QUANTIFIED

Compounds in Order of Gas Chromatographic
Elution on SE-52

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Naphthalene
Acenaphthene
Acenaphthylene
Fluorene
Phenanthrene
Anthracene
Methylantracenes/Methylphenanthrenes ^(a)
Fluoranthene
Pyrene
Methylpyrenes/Methylfluoranthenes ^(b)
Benzo(a)anthracene
Chrysene ^(b)
Methylchrysenes ^(b)
Dimethylbenzo(a)anthracene
Benzofluoranthenes ^(b)
Benzo(a)pyrene
Benzo(e)pyrene
Perylene
Indeno(1,2,3-cd)pyrene
Benzo(g,h,i)perylene
Coronene
Dibenzo(a,h)pyrene

(a) Summation of all isomers identified in sample excluding
internal standard: 9-methylantracene.

(b) Summation of all isomers identified in sample.

TABLE C-2. TOTAL PAH (mg) EMITTED IN WOOD STOVE EMISSIONS

Species Measured	Side Draft		Side Draft		Up Draft		Down Draft		High Turbulence	
	Oak-Seasoned	Particulate	Gas	Green	Oak-Seasoned	Particulate	Gas	Oak-Seasoned	Particulate	Gas
Naphthalene	1.2	65	0.22	80	0.16	11	0.07	52	0.36	62
Acenaphthene	0.12	58	0.27	89	0.10	18	0.12	51	0.60	31
Acenaphthylene	0.08	26	0.06	7.3	0.04	6.4	0.05	4.8	0.27	1.9
Fluorene	0.08	19	0.12	26	0.07	8.2	0.09	3.4	0.46	2.4
Phenanthrene	0.26	62	2.2	100	0.35	20	0.17	96	0.99	40
Anthracene	0.09	18	0.35	19	0.09	4.6	0.08	11	0.43	2.2
Methylanthracenes	0.07	3.2	0.13	7.4	0.07	1.4	-	2.0	0.33	0.99
Methylphenanthrenes										
Fluoranthene	2.6	18	2.9	11	0.30	9.1	0.12	68	0.73	15
Pyrene	2.8	8.6	3.1	6.1	0.28	6.8	0.07	38	0.46	9.6
Methylpyrenes/Methylfluoranthenes	0.79	0.53	0.63	0.82	0.16	1.9	-	2.6	0.30	1.5
Benzo(a)anthracene	5.9	1.0	3.0	0.22	0.39	13	0.16	6.1	0.96	1.8
Chrysene	5.6	1.1	3.2	0.21	0.37	8.2	0.11	8.5	0.73	1.9
Methylchrysenes	0.56	0.14	0.54	0.12	0.16	1.0	-	0.26	-	0.60
Dimethylbenzo(a)anthracene	0.29	-	0.28	-	0.09	0.25	-	0.13	-	-
Benzo(a)fluoranthene	14	0.96	21	0.15	1.3	17	0.11	3.7	0.93	0.86
Benzo(a)pyrene	3.5	0.24	7.1	0.08	0.42	3.8	0.07	0.48	0.50	0.43
Benzo(b)pyrene	5.0	0.27	13	0.08	6.3	6.5	0.07	0.20	0.50	0.40
Perylene	0.51	0.10	1.8	0.09	0.14	0.68	0.09	0.09	0.50	0.46
Indeno(1,2,3-cd)pyrene	15	0.29	38	-	1.3	3.9	0.17	0.15	1.1	0.80
Benzo(g,h,i)perylene	22	0.20	30	-	1.2	3.2	0.13	0.09	0.83	0.50
Coronene	10	0.11	16	-	0.51	0.55	0.17	-	0.86	0.63
Dibenz(a,h)pyrene	4.2	-	9.3	-	0.39	0.23	0.12	-	-	-
Total	95	263	154	346	14	146	2.0	351	12	175
Total Emission				502		160				

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In normal home operations, the cooling of flue gas on leaving the stove distribution system will cause an association and condensation of PAH with the discharged particulate matter. Thus stove emissions measured after discharge to the ambient air would be expected to have increased particulate-associated PAH concentrations.

As a general trend, observed in many combustion generated PAH samples, the amounts of high molecular weight PAHs are generally lower than the amounts of low molecular weight compounds. Phenanthrene was found to be a predominant species, a situation analogous to high phenanthrene concentrations found in coal combustion products. Benzo(a)pyrene and benzo(e)pyrene were produced in equivalent amounts except in the case of the up drafted stove burning seasoned oak, a situation where the benzo(a)pyrene content was appreciably higher.

The measured gas concentration and emissions of the PAHs are shown in Table C-3. The operating conditions of the stoves were shown in Table 2 of the report. Comparing stove burning modes, it is observed that PAH production was similar for different modes, with up draft producing slightly less total PAH than side or down draft. Green pine generated slightly higher levels of PAH than seasoned oak when the two fuels were burned in the same stove. The most significant reduction in total PAH was observed in the high turbulence furnace which evidently produced a highly efficient burn condition and greatly reduced PAH emissions.

Benzo(a)pyrene average concentrations and emissions were separately determined because of the special interest in this specie and its relatively high level of toxicity. The side draft mode produced slightly lower emissions of this specie when burning oak than the up draft burning mode. The down draft and high turbulence burning modes, however, resulted in significantly lower average emissions than the more conventional side draft and up draft modes. These benzo(a)pyrene average emissions were lower by one to two orders of magnitude.

A recent study of PAH emissions from residential wood combustion was reported by EPA.* Data from that program can be directly compared with

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* DeAngelis, D.G., Ruffin, D.S., Reznik, R.B., and Milliken, J.O., Preliminary Characterization of Emissions from Wood-Fired Residential Combustion Equipment, EPA-600/7-80-040, March, 1980, pg 60.

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TABLE C-3. COMPARISON OF STOVE OPERATING PARAMETERS
AND EMISSION FACTORS FOR PAH COMPOUNDS

Burn Mode Fuel	Side Draft Oak ^(a)	Side Draft Pine ^(b)	Up Draft Oak ^(a)	Down Draft Oak ^(a)	Turbu- lence Oak ^(c)
<u>Stove Parameters</u>					
Test Number	83	84	91a	80	91
Stove as modified	Defiant	Defiant	Riteway	Defiant	Dumont
Wood	dry oak	wet pine	dry oak	dry oak	dry oak
Shape	4x4	logs	4x4	4x4	logs
Flue gas temp., °F	700	590	950	710	340
Flue gas temp., °C	370	310	510	380	170
<u>Gas Composition</u>					
CO, percent	2.5	0.5	3.6	0.4	0.1
THC, ppm	6200	1800	7100	600	200
PAH, mg/m ³ (d)	300	390	110	250	89
BaP, mg/m ³	4.4	10	9.0	0.19	0.43
<u>Emissions</u>					
CO, lb/10 ³ lb wood	190	40	280	59	25
THC, lb/10 ³ lb wood	28	9	32	5	5
PAH, lb/10 ⁶ lb wood (d,e)	35	45	18	50	11
BaP, lb/10 ⁶ lb wood	0.52	1.2	1.4	0.038	0.053

- (a) Seasoned, triangular sawed pieces.
 (b) Green split logs.
 (c) Seasoned split logs.
 (d) Total PAH is defined as the sum of compounds quantified in this study (see Table C-1). Other PAH, substituted PAH and heteroatom containing fused ring compounds are potentially present but are not included in these measurements.
 (e) Equivalent to parts-per-million (W/W) based on the weight of wood burned.

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data from this study (see Table C-4) since test stoves were operated with similar fuels and similar operating parameters. In Table C-4, specific compounds and compound classes which were measured in both studies are compared as parts-per-million (W/W) of discharge based on the weight of fuel burned.

The data from these two studies show similar patterns for production of PAH although the earlier report found generally higher levels of total PAH. Both studies found that the lower molecular weight PAH were produced in larger amounts than larger molecules and both studies showed that anthracene and phenanthrene are a large fraction of the PAH produced. This finding suggests that benzene may be produced in significant amounts during residential wood combustion and future studies of wood combustion products should include this important suspect carcinogen in measurements.

The apparent difference in levels of PAH measured in the two studies can possibly be explained by differences in stove operating parameters or possibly by the difference between the packed column gas chromatographic technique used in the earlier report compared to the glass capillary method used in this study. The packed column can make integration of peak areas difficult due to coelution and peak overlap. Since these two studies were not conducted identically, the observed differences in PAH emissions are well within the variability of this type of emission measurement, and the variability in operating parameters for the stoves tested. Operating parameters are expected to be the major contributing factor to observed differences in PAH content, but consideration should be given to the lack of multiple tests required to establish the precision of reported data.

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TABLE C-4. COMPARISON OF REPORTED PAH EMISSIONS (mg/kg or lb/10⁶ lb Wood Fuel)

Stove Fuel	Baffled (a)		Non-Baffled (a)		Side Draft (b)		Up Draft (b)		Down Draft (b)		High Turbulence (b)	
	Oak (c)	Oak (c)	Oak (c)	Pine (d)	Oak (e)	Pine (d)	Oak (e)	Oak (e)	Oak (e)	Oak (f)	Oak (f)	Oak (f)
Compound (Class)												
Anthracene /	75		62	103								
Phenanthrene												
Methylanthracenes /	39		38	70								
Methylphenanthrenes												
Pyrene	16		17	19								
Methylpyrenes /	13		10	14								
Methylfluoranthenes												
Benzo(a)anthracenes /	13		7.6	1.3								
Chrysene												
Benzofluoranthenes	13		11	14								
Benzopyrenes / Perylene	8.3		8.4	9.4								
Indeno(1,2,3-cd)pyrene	0.07		-	-								
Benzo(g,h,i)perylene	4.5		4.3	4.8								
Total	180		160	240								

(a) Monsanto Report, EPA-600/7-80-040.

(b) This study.

(c) Seasoned.

(d) Green wood, split logs.

(e) Seasoned, triangular sawed pieces.

(f) Seasoned, split logs.

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